POTENTIAL *N*-NITROSODIMETHYLAMINE (NDMA) FORMATION FROM WATER TREATMENT POLYMERS

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POTENTIAL *N*-NITROSODIMETHYLAMINE (NDMA) FORMATION FROM WATER TREATMENT POLYMERS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

Amb SPE	Ambersorb solid-phase extraction
CSPE	Cartridge solid-phase extraction
DI	Deionized water
DMA	Dimethylamine
DMA-d_6	Dimethylamine-d_6
EI	Electron ionization
GC/MS	Gas chromatography/ mass spectrometry
LLE	Liquid-liquid extraction
NDMA	*N*-Nitrosodimethylamine
NDMA-d_6	*N*-Nitrosodimethylamine-d_6
PCI	Positive-ion chemical ionization
SPE	Solid-phase extraction
TOC	Total Organic Carbon
UDMH	Unsymmetrical Dimethylhydrazine
WW	Wastewater

SUMMARY

N-Nitrosodimethylamine (commonly known as NDMA) is a probable human carcinogen that has been recognized as an emerging drinking water contaminant in recent years. Previous studies have shown that certain N-containing organic compounds may form NDMA in reaction with chlorine or monochloramine and the NDMA yield is affected by the structure of the organic-N compounds, water conditions and treatment parameters. Many amine-based water treatment polymers contain organic-N functional groups and thus have been suspected as potential NDMA precursors in water treatment systems. The purpose of this research was to systematically assess the potential NDMA formation from different structural types of water treatment polymers in reactions with various oxidants and probe the possible factors that influence the NDMA formation. Robust analytical methods for detection of NDMA and the well-known NDMA precursor dimethylamine (DMA) in the reaction samples were established. The cationic polyacrylamide (cationic PAMS), aminomethylated polyacrylamide (Mannich), poly-diallyldimethylammonium chloride (polyDADMAC) and polyamine polymers were evaluated in reactions with nitrite, free chlorine, monochloramine or chlorine dioxide in aqueous solutions at circumneutral pH and room temperature conditions. This study employed high dosages of polymer and oxidant and long reaction time in order to assess the maximum potential to form NDMA. A range of operational parameters that may affect the above reactions were also evaluated.

CHAPTER 1

Introduction

1.1 Background of NDMA

N-Nitrosodimetylamine (NDMA) is a member of a chemical class, the N-nitrosamines, many of which are potential carcinogens. Although, no adequate studies of the relationship between exposure of NDMA and human cancer have been reported, NDMA is considered a probable human carcinogen based on supporting evidence of induced carcinogenicity in experimental animals [IARC, 1978 and 1987]. NDMA, when administered to rats and mice, has been shown to induce tumors in lung, liver, and kidney. NDMA is later identified by the US Environmental Protection Agency (EPA)'s Integrated Risk Information System [IRIS, 1991] as a human carcinogen and its carcinogenic properties are 1,000 times more potent than those of trihalomethanes.

NDMA is a semi-volatile, hydrophilic, and polar organic chemical. It is an oily yellow liquid of low viscosity with no distinct odor and highly soluble in water (reported solubility of 3,978 mg/L) [Wilczak et al., 2003]. NDMA is sensitive to light. The compound undergoes rapid photolytic degradation when exposed to ultraviolet light and decomposes in aqueous acid solutions. NDMA is not likely to bioaccumulate, biodegrade adsorb to particulate matter, or volatilize [Siddiqui and Atasi, 2001]. It is usually found at very low concentrations (ng/L, ppt) in the environment.

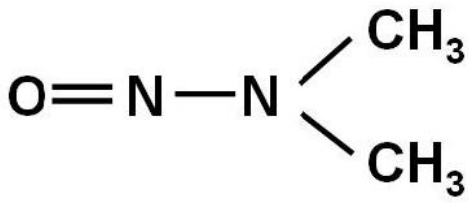

Figure 1.1 *N*-Nitrosodimethylamine (NDMA) structure

Table 1.1 Physical and chemical properties of *N*-Nitrosodimethylamine

Molecular Weight:	74.08
Density/Specific Gravity:	1.0048 at 20 ºC (water = 1)
Boiling Point:	151 – 153 ºC
Vapor Density:	2.56 (air = 1)
Vapor Pressure:	2.7 mm Hg at 20 ºC
Log Octanol/Water Partition Coefficient:	-0.57
Synonyms: dimethylnitrosamine; *N*-methyl-*N*-nitrosomethanamine; DMN; DMNA	

(Source references: Merck, 1983; HSDB, 1993; US EPA 1994a)

NDMA was used in a number of applications historically. It was used as a solvent in the fiber and plastics industry, a plasticizer for rubber and acrylonitrile polymers, an antioxidant, an additive for lubricants, a softener of copolymers and a research chemical and in inhibition of nitrification in soil, in the preparation of thiocarbonyl fluoride polymers, and in other uses [Merck, 1983]. From the mid 1950's to 1976, NDMA was used as an intermediate in the electrolytic production of 1,1-dimethylhydrazine, storable liquid rocket fuel that contained approximately 0.1% NDMA as an impurity. Although

current production data of NDMA were not available, this compound is no longer believed to be commercially manufactured in the United States.

NDMA has been found in wastewater effluents and sludges, diesel and gasoline engine exhausts, rubbers, chemicals, dyes, and leathers. It is also present in a variety of foods and beverages including cheeses, canned fruit, various meat products, and beers, and in tobacco smoke, cosmetic products, herbicides, and pesticides.

1.2 Regulatory Considerations

Although NDMA is listed on the priority pollutant list [CFR, 2001], there is no establishment of a federal maximum contaminant level (MCL) yet for this compound. However, many regulatory agencies have established their own NDMA guidelines. The Office of Environmental Health Hazard Assessment (OEHHA) and US EPA have estimated 10^{-6} lifetime risk level of cancer from NDMA exposures at 0.7 ng/L. In 1992, the Ontario Ministry of the Environment and Energy (OMOE) established an Interim Maximum Acceptable Concentration (IMAC) of 9 ng/L for NDMA which was later changed to a drinking water standard in 2000 [Barrett et al., 2003]. The California Department of Health Services (CDHS) initially set a drinking water action level (AL) for NDMA at 2 ng/L and later revised to an advisory level of 10 ng/L in 2002 after the discovery of widespread presence of NDMA as a byproduct of chlorination and chloramination in drinking water [CDHS, 2002]. As concern over NDMA as an emerging disinfection byproduct continues to increase, regulation of this compound is likely in the future.

1.3 NDMA Occurrence in Water and Wastewater Treatment Plants

NDMA was first observed in municipal drinking water in Ontario, Canada in 1989 [Mitch et al., 2003b], which prompted a survey for NDMA concentrations in 145 drinking water treatment plants (DWTPs) [Jobb et al., 1994; MOE, 1998]. The results showed that NDMA levels in the treated water from most of the plants were less than 5 ng/L. In 2001, the CDHS conducted a NDMA survey in effluents of 20 DWTPs [CDHS, 2002]. The results showed that the treated water from 3 of the 20 plants surveyed contained NDMA at greater than 10 ng/L. All eight DWTPs that used only free chlorine in water disinfection showed NDMA levels less than 5 ng/L. However, one of the four DWTPs that involved anion exchange in the treatment showed NDMA concentration exceeding 10 ng/L. During 2001, a North American survey of NDMA in 21 water systems indicated the median NDMA concentration in treated effluents was less than 1 ng/L. The median NDMA concentration from distribution systems was less than 2 ng/L for chloraminated water and less than 1 ng/L for chlorinated water. High NDMA levels were found in groundwater treated with anion exchange resins and chlorination, and in groundwater treated with lime softening and chloramination. More samples with NDMA concentrations between 2.5 and 10 ng/L were found in chloraminated systems than in chlorinated systems [Barrett et al., 2003].

In contrast to the results from drinking water treatment plants, effluents from conventional wastewater treatment plants may contain relatively high NDMA concentrations. Large increases in NDMA concentrations were attributed to upstream industrial sources. Typical NDMA levels found in unchlorinated secondary effluents are

less than 20 ng/L, but industrial inputs can elevate NDMA concentrations in raw sewages to be above 1000 ng/L. For example, effluents from printed circuit board manufacturing processes using NDMA-contaminated dimethyldithiocarbamate have been reported to contain NDMA concentrations up to 105,000 ng/L [OCSD, 2002]. In addition to industrial input, NDMA may be generated during chlorination or chloramination of wastewater [Choi and Valentine, 2002a and 2002b].

1.4 Treatment Alternatives for NDMA

A number of treatment methods have been tested for removing NDMA from water. Conventional water treatment processes such as air stripping, activated carbon adsorption and biodegradation are ineffective in removing NDMA due to the chemical nature of this compound [Merck, 1983; HSDB, 1993; US EPA 1994a]. Neither full-scale air strippers nor full-scale granular activated carbon (GAC) contactors designed for volatile organic compound (VOC) removal from groundwater showed significant ability to remove NDMA [Montgomery, 1998]. The treatment technologies that are more likely to remove NDMA include ultraviolet (UV) irradiation, UV oxidation, and resin adsorption [Wong, 2000].

NDMA is known to degrade in the presence of UV light, which makes it a good candidate for removal by UV irradiation treatment. UV irradiation is now a commonly used treatment process for removal of NDMA and has been shown to reduce NDMA in groundwater to very low levels (ppt) [Wong, 2000]. However, possible harmful by-products may emerge from this treatment. UV irradiation of NDMA is suspected to

produce dimethylamine, a well-known NDMA precursor [Choi and Valentine, 2002a; Mitch and Sedlak, 2002b], and the photolysis of any nitrate in water may increase nitrite (NO_2^-) concentration, also a suspected reagent to generate NDMA via nitrosation reactions [Choi and Valentine, 2003b]. Therefore, reformation of NDMA after destruction by UV irradiation may be possible if there are suitable organic precursors in the water, a scenario especially probable in the case of wastewater. The disinfection processes, chlorination and/or chloramination following UV irradiation were suspected of causing NDMA reformation. As a result, all treatment applications should occur before the UV treatment to ensure the effectiveness of this process.

The combination of UV light and an oxidant such as hydrogen peroxide is commonly used in advanced oxidation processes. However, the addition of hydrogen peroxide can hinder UV treatment since the peroxide can filter out UV light. For NDMA treatment, the use of UV light alone is more effective than UV/H_2O_2 oxidation. However, if other contaminants are also present in the water, the UV/H_2O_2 oxidation may be considered for combined treatment [Wong, 2000].

Resin adsorption is another promising method for NDMA treatment. A carbonaceous resin, Ambersorb 572, has been shown to be the most effective material for NDMA removal [Wong, 2000]. In fact, the Ambersorb 572 resin has been commonly used in NDMA analysis. It is so far the most effective NDMA adsorbent and is widely used in solid-phase extraction for NDMA.

CHAPTER 2

Literature Review

2.1 NDMA Formation in Drinking Water and Wastewater

High concentrations of NDMA have been observed in industrial wastewater effluents due to industrial inputs and NDMA-contaminated chemicals used in the manufacturing processes [OCSD, 2002]. However, recent studies have shown that NDMA can be formed at significant levels in both chlorinated drinking water and wastewater (e.g., reviewed in Mitch et al., 2003b). The results suggest that NDMA is a water treatment byproduct especially associated with disinfection processes. Currently, two formation pathways have been proposed to be responsible for NDMA formation in drinking water and wastewater: (i) formation of NDMA via *N*-nitrosation reaction, and (ii) formation of NDMA by oxidation of an unsymmetrical dimethylhydrazine (UDMH) intermediate. Details of these two proposed formation mechanisms are discussed below.

2.1.1 N-Nitrosation: NDMA Formation via Nitrite

As shown in reactions (1) and (2), the *N*-nitrosation mechanism involves the formation of nitrosyl cation or similar nitrogen-containing species during acidification of nitrite. The nitrosyl cation then reacts with amine species, such as DMA, to form NDMA [Mirvish, 1975; Choi and Valentine, 2003b]. The nitrosation reaction undergoes most

rapidly in acidic environments, especially near pH 3.4 [Mirvish, 1975]. During this reaction, the demands for protonation of nitrite (pK_a of nitrite = 3.35) and high fraction of unprotonated dimethylamine (pK_a of DMA = 10.7) counter against each other in terms of pH requirement. Overall, the need for protonation of nitrite is especially critical for the rate of the nitrosation reaction.

$$HNO_2 + H^+ \leftrightarrow H_2O + NO^+ \quad (1)$$

$$NO^+ + (CH_3)_2NH \rightarrow (CH_3)_2N - N = O + H^+ \quad (2)$$

The nitrosation mechanism is believed to be responsible for NDMA occurrence in many food products such as meat products cured with nitrite, cigarette smoke, malt beverages, and dried foods [Mitch et al., 2003b]. Although nitrosation reaction occurs slowly at neutral and basic pH, several studies have reported that photochemical reactions [Ohta et al., 1982], formaldehyde [Keefer and Roller, 1973] and fulvic acid [Weerasooriya and Dissanayake, 1989] can catalyze nitrosation at circumneutral pH. Recently, Choi and Valentine (2003) reported that the formation of NDMA by nitrosation of DMA can be greatly enhanced by the presence of free chlorine during water chlorination processes. The authors attributed the enhancement effect to the formation of a highly reactive nitrosating intermediate such as dinitrogen tetroxide (N_2O_4) during oxidation of nitrite to nitrate by free chlorine.

2.1.2 Unsymmetrical Dimethylhydrazine (UDMH) Oxidation

Earlier studies have reported that NDMA can be produced from oxidation of 1,1-dimethylhydrazine or unsymmetrical dimethylhydrazine (UDMH) by hypochlorite [Brubaker et al., 1985 and 1987], cupric ions [Banerjee et al., 1984], hydrogen peroxide, and oxygen [Lunn et al., 1991]. Because NDMA is formed when UDMH is oxidized, it had been hypothesized that any chlorination reactions that produce UDMH should produce NDMA. Recent studies by Mitch and Sedlak (2002b) and Choi and Valentine (2002a and 2002b) provided experimental evidence supporting that the UDMH oxidation pathway might be responsible for NDMA formation involving chloramine species. As illustrated in Figure 2.1, this pathway includes the slow formation of UDMH from the reaction of monochloramine and DMA, followed by rapid oxidation of UDMH by monochloramine or other oxidants present in water. When the UDMH intermediate is oxidized, it produces NDMA at low yields (< 1%) [Mitch and Sedlak, 2002b]. Due to the slow kinetics of the UDMH formation step, the overall NDMA formation reaction is quite slow and may occur over a period of several days. The UDMH oxidation pathway is highly dependent on water pH and exhibits the fastest reaction rate near circumneutral pH [Mitch and Sedlak, 2002b; Mitch et al., 2003b].

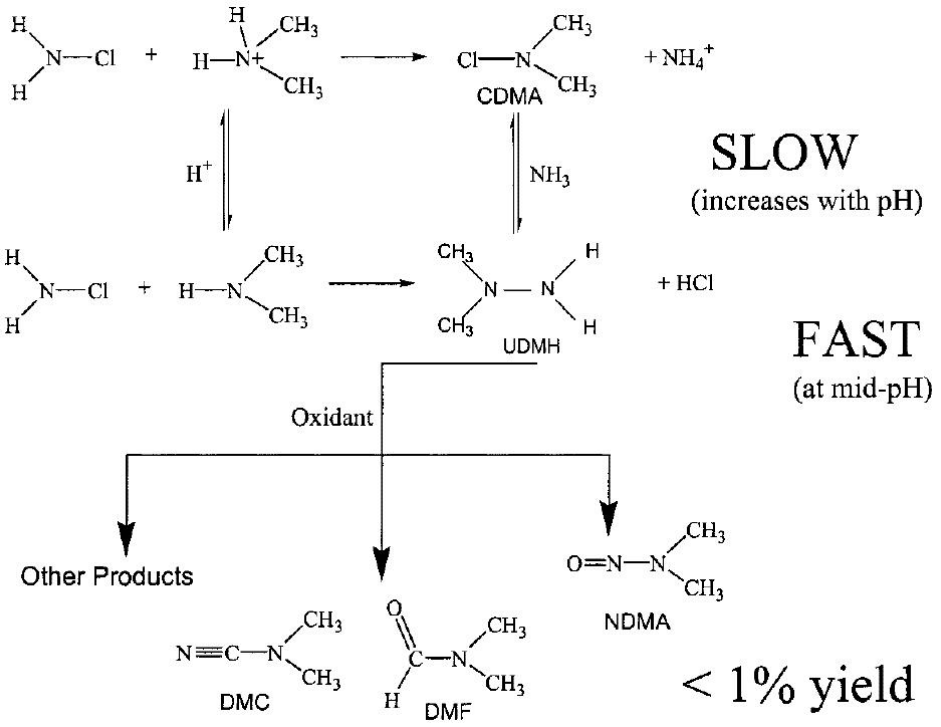

Figure 2.1 NDMA formation from UDMH oxidation [from Mitch and Sedlak, 2002b]

2.2 Potential Precursors for NDMA and Other Nitrosamines

On the basis of the nitrosation and UDMH oxidation pathways described above, it is conceivable that the structures of the precursor amines play a significant role in the overall NDMA formation potential. Thus far, DMA has been shown by many studies to be a very effective NDMA precursor (e.g., Fiddler et al., 1972; Mitch and Sedlak, 2002b; Choi and Valentine, 2002a). However, it is also recognized that DMA concentration alone is not sufficient to account for NDMA formation in real water samples such as secondary wastewater effluent [Mitch and Sedlak, 2003c].

The earlier work by Fiddler et al. (1972) showed the formation of NDMA from naturally occurring quaternary ammonium compounds and tertiary amines via nitrosation

reactions. The more recent studies by Mitch and Sedlak (2002b and 2004) reported that aliphatic tertiary amines that contained dimethylamine functional groups (e.g., trimethylamine and dimethylethanolamine) could serve as NDMA precursors in reactions with monochloramine but at a lower yield than DMA (roughly half of that formed by DMA). The lower yield of NDMA formation from the tertiary amines is likely due to the need to break a C-N bond prior to NDMA formation. In their studies, the authors also reported that monomethylamine (a primary amine), tetramethylamine (a quaternary amine), dimethylamides, amino acids, amino sugars, and proteins did not form significant levels of NDMA.

More structurally complex amines or amine-containing compounds have also been suspected as NDMA precursors due to their potential to release DMA. The fungicide dithiocarbamates contain hydrolysable dimethylamine groups and have been shown to be good NDMA precursors [Brubacher et al., 2003]. On the similar basis, the amine-based anion-exchange resins and coagulant/flocculant polymers commonly used in water treatment facilities are also suspected NDMA precursors and are discussed further in the following section.

Furthermore, studies also observed formation of other members of *N*-nitrosamines from their corresponding precursor amines, presumably via similar pathways as those for NDMA formation. For example, diethylamine and dipropylamine may form *N*-nitrosodiethylamine (NDEA) and *N*-nitrosodipropylamine (NDPA) in reactions with monochloramine, respectively [Mitch and Sedlak, 2003c]. The cancer potencies of NDEA and NDPA are comparable to that of NDMA according to the EPA IRIS database. Monitoring the formation of other nitrosamines may become important in the future if

inclusion of these compounds into exposure and risk assessment is determined to be necessary by health officials and regulatory agencies.

2.3 Potential NDMA Formation Related to Treatment Polymers

The use of ion-exchange resins for water purification was reported by Kimoto et al. (1980) to cause NDMA formation when tap water containing residual chlorine was passed through the resins. The author hypothesized that the quaternary ammonium groups present in the resins were acting as NDMA precursors. A study by Najm and Trussell (2001) showed that the composition of the anion-exchange resins may affect the level of NDMA formed. Four types of strong-base anion-exchange resins were used in the above study. The dimethyl quaternary amine resin resulted in a much greater amount of NDMA when compared to other resins with longer chain substitutes (i.e., trimethyl-, triethyl-, and tripropylamines).

An earlier study by Child et al. (1996) found that NDMA was formed when dimethylamine-containing polymer (i.e., a poly-diallyldimethylammonia chloride (DADMAC) polymer, structure shown in Figure 2.2) was reacted with high concentration of chlorine. However, contact between typical doses of chlorine and the polymer under water treatment conditions did not form measurable levels of NDMA. A later study by Najm and Trussell (2001) reported that the contact of polyDADMAC polymer with chlorine under typical water treatment conditions did not produce significant level of NDMA (< 2 ng/L). PolyDADMAC polymers are used extensively in drinking water treatment as cationic coagulant aids. They have proven to greatly improve the coagulation and flocculation efficiency of inorganic aluminum and ferric coagulants.

On the contrary, the studies by Wilczak et al. (2002 and 2003) showed that chloramination of DADMAC cationic polymer solution formed significant levels of NDMA. In their study, the NDMA concentration increased with higher dosage of the cationic polymer in general. The recent work by Najm et al. (2004) investigated NDMA formation from polyDADMAC and polyacrylamide polymers. Higher amounts of DMA release, as well as higher levels of NDMA formation were found from the cationic DADMAC polymers than from the non-ionic polyacrylamide polymers under chloramination conditions. DMA release and NDMA formation were also proportionally related to the concentration of the DADMAC cationic polymers. The study results also showed that increased chlorine contact time prior to ammonia addition only increased NDMA formation slightly. However, NDMA formation increased with increasing contact time with monochloramine and with increasing monochloramine concentration.

The study by Mitch and Sedlak (2004) reported that a polyacrylamide polymer containing tertiary amines with dimethylamine functional group (structure shown in Figure 2.2) produced high levels of NDMA after being in contact with monochloramine. In contrast, another polymer that contained quaternary amine functional groups, i.e., *N*,*N*,*N*-trimethyl-2-[(1-oxo-2-propenyl]oxy]ethanaminium-based polyacrylate cationic polymer, also known as an ADAMQUAT polymer (structure shown in Figure 2.2), did not generate much NDMA. The authors suggested that the lack of a free lone pair on the nitrogen atoms of the quaternary amine functional groups likely hindered a reaction with the monochloramine electrophile, in a similar fashion to the poor nitrosation reaction of quaternary amines. When commenting on the previous studies that reported formation of NDMA from polymers or resins containing quaternary amine functional groups, the

authors suspected that the observed formation might involve reaction of chlorine with tertiary amine precursors present as impurities in the resin or as resin degradation products. Additionally, a polyacrylate anionic polymer (structure shown in Figure 2.2) was shown in the same study to yield negligible amount of NDMA during chloramination.

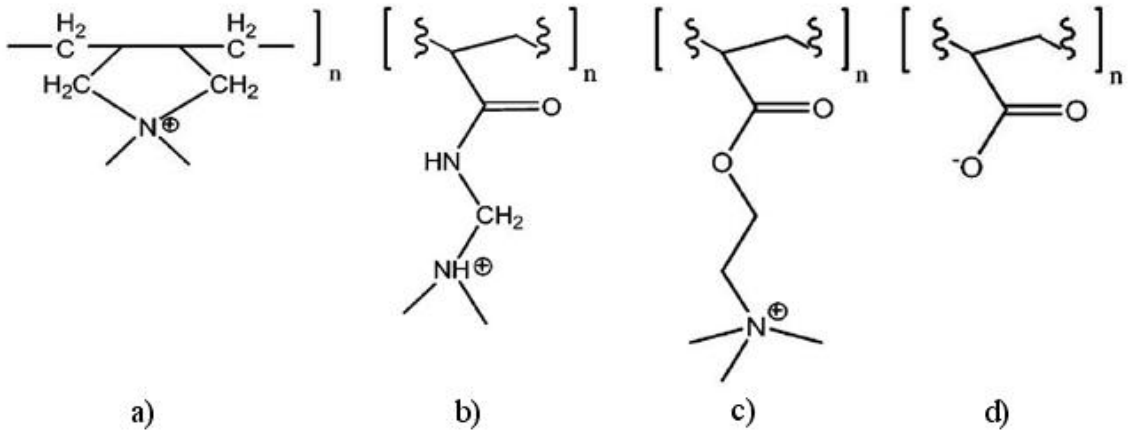

Figure 2.2 Chemical structures:
a) diallyldimethylammonium-based cationic polymer (DADMAC);
b) dimethylamine-based polyacrylamide cationic polymer;
c) *N*,*N*,*N*-trimethyl-2-[(1-oxo-2-propenyl]oxy]ethanaminium-based polyacrylate anionic polymer (ADAMQUAT polymer) and
d) polyacrylate anionic polymer

[from Mitch and Sedlak, 2004]

2.4 Effect of Water Quality and Treatment Parameters

The abundance and structural property of organic precursors in waters and the concentration of monochloramine and nitrite apparently influence the levels of NDMA formation. Water conditions (e.g., pH, NOM, the presence of bromide, the presence of other chlorine scavengers, etc.) and treatment parameters (e.g., contact time, types and sequence of treatment processes) also affect NDMA formation. The available data show that most organic-N precursors form NDMA slowly with low yields. As a result, all studies showed an increase of NDMA levels when extending the contact time (from hours to several days). The slow kinetics of NDMA formation can result in a lower amount of NDMA being formed during the treatment residence time, but may lead to growing NDMA formation within the water distribution systems when monochloramine and/or nitrite are also present. Considerably high concentrations of NDMA levels were observed in filter backwash effluent, suggesting that filter cleaning process could produce spikes in NDMA levels [Wilczak et al., 2003]. Other constituents of water may act as catalysts or inhibitors for NDMA formation. For instance, bromide in water can facilitate NDMA formation in reactions between amine precursors and monochloramine [Choi and Valentine, 2003a]. Presence of other chlorine scavengers in water may also reduce the amount of NDMA being formed.

2.5 Analysis of NDMA

The analytical procedure to detect NDMA may involve several steps from sample collection, preconcentration to analysis. Currently, standard analytical methods for low concentrations of NDMA in drinking water have not been established. A common technique used for analysis of NDMA is the utilization of liquid-liquid extraction to extract NDMA from water, followed by detection using gas chromatography with tandem mass spectrometry in the chemical ionization mode (GC/CI/MS/MS) [Eaton and Briggs, 2000; Mitch and Sedlak, 2002b] or gas chromatography with high resolution mass spectrometry (GC/HRMS) [Taguchi et al., 1994]. Typical detection limits of these methods were around 1 ng/L. The liquid-liquid extraction (LLE) with methylene chloride using separatory funnels can be applied in NDMA extraction according to the US EPA Method 3510C [US EPA, 1998b]. However, this method often yielded low recoveries when used with wastewater effluents. The separations between effluents and methylene chloride were hindered by constituents in the effluents such as surfactants which may cause emulsion-like environments [Mitch et al., 2003b]. Alternatively, continuous liquid-liquid extraction (CLLE) according to the US EPA Method 3520C [US EPA, 1998b] could be employed to avoid problems associated with emulsions encountered in traditional LLE. The CLLE method reportedly yielded extraction efficiencies up to 60% [Mitch et al., 2003b].

The LLE methods are labor intensive and require the use and disposal of large volumes of methylene chloride solvent, rendering these methods inconvenient and less environmental friendly for routine analysis. As concerns over NDMA in water supplies increase, more monitoring of this contaminant is quite likely in the future. Improved

analytical methods that are more sensitive, reliable, and economically attainable for measuring low concentrations (at several ppt or even lower) of NDMA in water are much needed. Solid-phase extraction (SPE) has been developed as an alternative method because it possesses several advantages over LLE such as lower costs, shorter extraction times, accommodation of more samples, ease of practice and optimization. For example, a study described by Tomkins and Griest (1996) employed a solid-phase extraction using a carbon-based Empore SPE disk which resulted in as high as 60% in NDMA recovery.

Analysis of NDMA is usually based on isotope dilution, a technique that involves spiking the deuterated isotopic form of NDMA (i.e., NDMA-d_6) into the sample as an internal standard for quantification [Taguchi et al., 1994]. This technique is particularly suitable for GC/MS since mass spectrometry can readily distinguish the different mass-to-charge ratios (m/z) of the parent compound and its isotopic analogue, and utilization of isotope internal standards precludes potential background contamination from natural sources. Detection of NDMA is typically conducted by either electron ionization (EI) or positive-ion chemical ionization (PCI) using selected ion monitoring (SIM) mode. Compared to PCI, EI may lack selectivity and yield fragmentation patterns that are not most favorable. PCI uses a softer ionization process, causes less molecular fragmentation, and may enhance selectivity and sensitivity for analytes [Prest and Herrmann, 1999]. Alternatively, high-resolution mass spectrometry (HRMS) may be used to increase selectivity under the EI mode. Utilization of large-volume injection (LVI) may also be applied to lower the concentration of NMDA that can be detected in extracted samples.

2.6 Research Objectives

As summarized in the above literature review, a significant number of studies have indicated that certain water treatment polymers may be NDMA precursors under water chloramination or chlorination conditions. However, results up-to-date are still far from being comprehensive or systematic. The mechanisms of which NDMA is formed from the polymers and what the critical influencing factors are for the NDMA formation are still poorly understood.

The purpose of this research is to conduct a systematic experimental investigation to assess the potential NDMA formation from four different structural types of water treatment polymers and probe the possible factors that influence such a formation. The specific research objectives in this study are to:

1. Establish robust and sensitive analytical methods for detection of NDMA and DMA.
2. Evaluate potential NDMA formation from four types of widely used water treatment polymers: cationic polyacrylamide, aminomethylated polyacrylamide (Mannich), poly-diallyldimethylammonium chloride (polyDADMAC), and polyamine in reactions with typical water disinfection oxidants including chlorine, monochloramine, chlorine dioxide, and nitrite.
3. Evaluate whether the above treatment polymers are stable under water treatment conditions and storage conditions, particularly with respect to DMA release.
4. Evaluate the effect of water quality conditions and treatment parameters on the formation of NDMA from the water treatment polymers.

5. Identify the critical factors that influence the formation of NDMA from water treatment polymers.

CHAPTER 3

Materials and Methods

3.1 Materials

Deionized (DI) water used in the experiments was produced from a Millipore Milli-Q Nanopure water purification system. A.C.S. reagent grade water from Sigma-Aldrich was used to prepare dimethylamine standard solutions and preformed monochloramine stock solutions. Dimethylamine hydrochloride (99%), sodium nitrite (98+%), 4-methoxybenzenesulfonyl chloride (99%) and sodium thiosulfate were obtained from Acros. Ammonium chloride (99.9%), ferrous ammonium sulfate, sodium hypochlorite (4-6%, purified grade), potassium iodide dibasic, potassium phosphate, *N*,*N*-diethyl-p-phenylenediamine oxalate, disodium ethylenediamine tetraacetate (EDTA) were obtained from Fisher Scientific. The above reagents were used directly without further purification. *N*-nitrosodimethylamine from Protocol Analytical, and *N*-nitrosodimethylamine-d6 (98%), and dimethylamine-d6 (98%) from Cambridge Isotope Laboratories were used as standards without further purification. Sodium bicarbonate (99.7+%), sodium phosphate monobasic (99%), and sodium phosphate dibasic (99.7%) (from Fisher Scientific) were used to produce buffer stock solutions. Small amounts of sulfuric acid and sodium hydroxide (from Fisher Scientific) were further added to buffered solutions to adjust pH to a specific value. L-ascorbic acid (99+%) from Fisher Scientific was used for quenching. Solvents used in experiments were Fisher Scientific

acetone for derivatizing solution, methanol for standard dilutions and washing, and methylene chloride for liquid-liquid extractions, solid-phase extractions and GC/MS analyses. Supelco Ambersorb 572 adsorbent was used to extract NDMA from water samples and Environmental Express TCLP non-binding borosilicate microfiber filters with a nominal pore size of 0.7 μm were used to filter samples.

3.2 Preparation of Monochloramine Stock Solution

Monochloramine solution was prepared in 4 mM bicarbonate buffer by adding sodium hypochlorite slowly into an ammonium chloride solution. Ammonium chloride was first dissolved in DI water and adjusted with NaOH to pH 9.5. Then a predetermined amount of sodium hypochlorite solution was added by drops slowly into the rapidly stirred ammonium chloride solution at Cl/N molar ratio of 0.7. The solution pH was maintained at 9.5 or slightly higher during the reaction to minimize disproportionation of monochloramine to dichloramine. The solution was stored in dark amber glass bottle and stirred for at least two hours before use. This preformed monochloramine solution was used within one day. The concentration of monochloramine was determined by the DPD-FAS titration method specified in the Standard Methods for the Examination of Water and Wastewater [APHA, 1998].

3.3 Preparation of Chlorine Dioxide Stock Solution

Chlorine dioxide solution was generated by slowly adding 100 mL of 8.0 N sulfuric acid (H_2SO_4) to 250 mL of 160 g/L sodium chlorite ($NaClO_2$) solution under constant stirring (modified from Pitochelli, 1995). The reactor was set up with air

continuously bubbling in through an inlet and leaving via an outlet. The reaction between sulfuric acid and sodium chlorite produced chlorine dioxide gas, which was captured in solution by passing through chilled DI water. The same reaction was repeated again and the generated chlorine dioxide gas was trapped in the same chilled DI water trapper. The final yellow solution of chlorine dioxide was then stored in an amber glass bottle and kept in a refrigerator. Prior to each use, the concentration of chlorine dioxide was determined by titrating with sodium thiosulfate in the presence of potassium iodide, acid and starch indicator as specified in the Standard Methods [APHA, 1998].

3.4 NDMA Analysis

NDMA was determined using solid-phase extraction followed by isotope dilution gas chromatography/mass spectrometer (GC/MS) method [Taguchi et al., 1994]. All glassware was cleaned with Micro brand laboratory detergent, rinsed with methanol and DI water, and prebaked at 300 °C for at least 3 hours prior to use in each analysis to eliminate any organic residues or contaminants. Typically, ten microliters of 5 mg/L deuterated NDMA (NDMA-d_6) stock solution was spiked into a 500-mL water sample as an internal standard (100 ng/L). After adding the internal standard, 200 mg of Ambersorb 572 beads (pre-conditioned at 300 °C for 3 hours prior to use) was added to the sample to extract NDMA. The samples were placed on a platform shaker at 175 rpm for 3 hours to extract NDMA. After extraction, the samples were filtered and the Ambersorb beads were collected on a non-binding borosilicate fiber filters, air-dried at room temperature for one hour and transferred to a 2-mL amber vial. Methylene chloride (400 μL) was added to the vial to desorb NDMA from the Ambersorb beads. The vials were immediately capped and

tapped for 30 min before loading onto the autosamplar tray for GC/MS analyses. To prepare calibration standards, NDMA and NDMA-d_6 were dissolved in methylene chloride at 20-1000 μg/L and 25-500 μg/L, respectively.

NDMA was analyzed using an Agilent GC/EI/MS (6890/5973) system with a HP-5MS column (30 m × 250 μm × 0.25 μm). NDMA analysis method used spitless injection of 2 μL with an injection port temperature of 200 °C, a transfer line temperature of 260 °C and an MSD ion source temperature of 150 °C. The GC temperature conditions modified from Mitch et al. (2003a) were: held at 35 °C for 1 min, ramped at 10 °C/min to 70 °C, ramped at 2 °C/min to 72 °C, and then ramped at 15 °C/min to 240 °C, with a final hold at 2.4 min. NDMA and NDMA-d_6 were both quantified in selected ion monitoring mode (SIM) using m/z 74.1 as parent and m/z 42 as daughter ions for NDMA and m/z 80.1 as parent and m/z 48 as daughter ions for NDMA-d_6 (Figure 3.1). The relative abundance of the daughter ion to the parent ion is similar in both NDMA and NDMA-d_6. Calibration curves for quantification were based on the parent ion and yielded linear relationships throughout the employed concentration range ($R^2 > 0.99$). The existence of the daughter ion at the correct relative abundance and the corresponding chromatographic retention time were used, in addition to the parent ion, to verify the identities of NDMA and NDMA-d_6 in the samples.

The typical extraction recoveries of NDMA-d_6 were 20-60% depending on sample matrices. The final reported concentration of NDMA was after adjustment by the concentration factor (C.F. = 1,250 typically) and the corresponding NDMA-d_6 recovery in the sample. The method detection limit for NDMA analysis was approximately 15 ng/L or higher based upon the sample matrix involved.

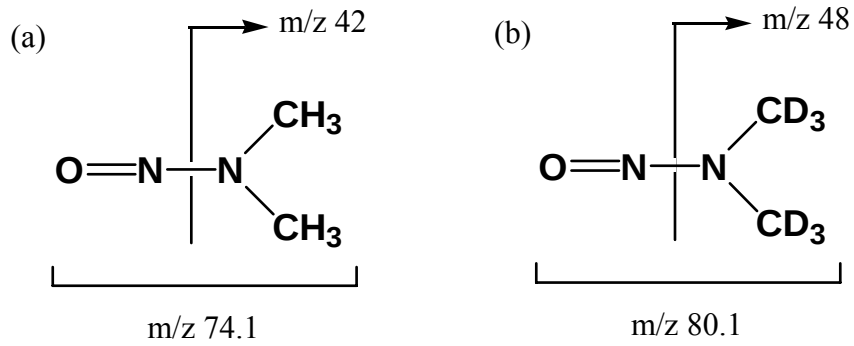

Figure 3.1 Structures and fragmentation of a) *N*-Nitrosodimethylamine and b) *N*-Nitrosodimethylamine-d_6

3.5 Dimethylamine Analysis

Dimethylamine (DMA) was analyzed using a modified method from Mitch and Sedlak (2003a). Ten microliters of 0.2 µg/µL deuterated dimethylamine (DMA-d_6) stock solution in methanol was added as an internal standard to a 100-mL sample, resulting in a final 2 µg/L of spiking concentration. Fifty millimolar of phosphate buffer was added to the solution to maintain pH at 7.5. One hundred microliter of 4-methoxybenzenesulfonyl chloride in acetone (0.5 g/mL stock solution) was added as the derivatizing agent as shown by the reaction in Figure 3.2. The solution was stirred for 3 hours and extracted twice using 20 mL of methylene chloride (2 min in a separatoy funnel) followed by a back-extraction with 40 mL of DI water in a separatory funnel for 1.5 min. The extracted methylene chloride was then concentrated down to a final volume of 1 mL under mild heating or a gentle nitrogen gas stream, and transferred to amber glass vials. Calibration standards of DMA and DMA-d_6 were prepared by dissolving these two compounds at

0.1-50 µg/L in DI water, followed by the derivatization and extraction steps described above.

The samples were analyzed by an Agilent GC/EI/MS instrument as described in the previous section. The GC oven temperature conditions began at 100 °C, held for 1 min and then ramped at 8 °C/min to 250 °C and held at 250 °C for 3 min. DMA and DMA-d_6 were quantified in SIM mode using the m/z 215 parent and m/z 171 daughter ions for DMA, and the m/z 221 parent and m/z 171 daughter ions for DMA-d_6. Quantification was also primarily based on the parent ion and yielded very linear calibration curves (R^2 > 0.98). The typical recoveries of DMA-d_6 were 60-90% depending on sample matrices. The final reported concentration of DMA was after adjustment by the concentration factor (C.F. = 100 typically) and the corresponding DMA-d_6 recovery in the sample. The detection limit for DMA was approximately 0.1 µg/L.

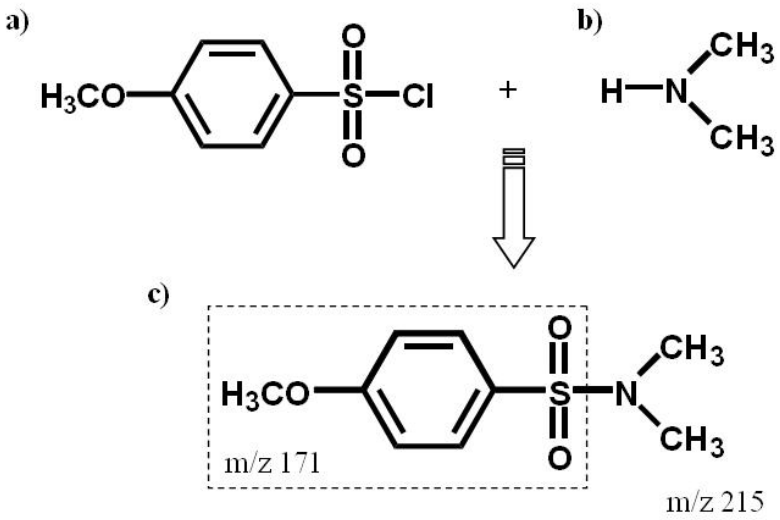

Figure 3.2 Structures of a) 4-methoxybenzenesulfonyl (derivatizing agent), b) dimethylamine (DMA) and c) derivatized DMA

3.6 Investigation of Solid-Phase Extraction (SPE) Efficiencies

In the initial stage of this study, two different solid-phase extraction methodologies were investigated: the cartridge SPE (CSPE) method and the free Ambersorb 572 resin SPE (Amb SPE) method. The traditional Amb SPE was first introduced by Taguchi et al. in 1994 as an alternative to liquid-liquid extraction. Among several carbonaceous materials that the authors examined, the Ambersorb 572 adsorbent was the most efficient material in extracting NDMA. Instead of using in the form of loose particles, the solid-phase adsorbent materials can be pre-packed into a cartridge which can be used to extract analytes by passing the water sample through the cartridge by a pump. Such method development has been reported by several research groups [Tomkins et al., 1995; Charrois et al., 2004; Cheng et al., 2005].

3.6.1 Cartridge Solid-Phase Extraction (CSPE)

Three different types of commercial cartridges, Waters Oasis-HLB, Phenomenex Strata-X, and Supelco Envi-18 were examined to determine whether they could achieve desirable NDMA extraction efficiencies. These cartridges are particularly suitable for polar compounds and have been used widely for polar contaminants such as antibiotics [Renew and Huang, 2004]; therefore they were hypothesized to be suitable adsorbent for NDMA. According to the information provided by the manufacturers, the Oasis-HLB cartridges contain a unique copolymer specifically designed to be hydrophilic-lipophilic balanced (HLB), which give high and reproducible recoveries over the wide range of pH. The Strata-X cartridges have high surface area, good pH stability and suitable for adsorption and extraction of polar compounds. The Envi-18 cartridges also have high surface area and are used to extract many pesticides.

The cartridges were tested for extracting NDMA using a solid-phase extraction apparatus shown in Figure 3.3. Ten microliters of NDMA stock solution in methanol were spiked into a 1-L sample (final 100 ng/L). The cartridges were conditioned with 2 mL of methanol and then 2 mL of DI water prior to use. The water samples were steadily passed through the cartridges by vacuum suction. Afterwards, the cartridges were eluded with 10 mL of methylene chloride followed by nitrogen blowdown to reduce the final volume to 2 mL. The concentrated samples were then transferred to amber glass vials for GC/MS analyses. The results showed that all three cartridges yielded poor recoveries for NDMA at 0.9, 1.7, and 2.8% for Oasis-HLB, Strata-X, and Envi-18, respectively.

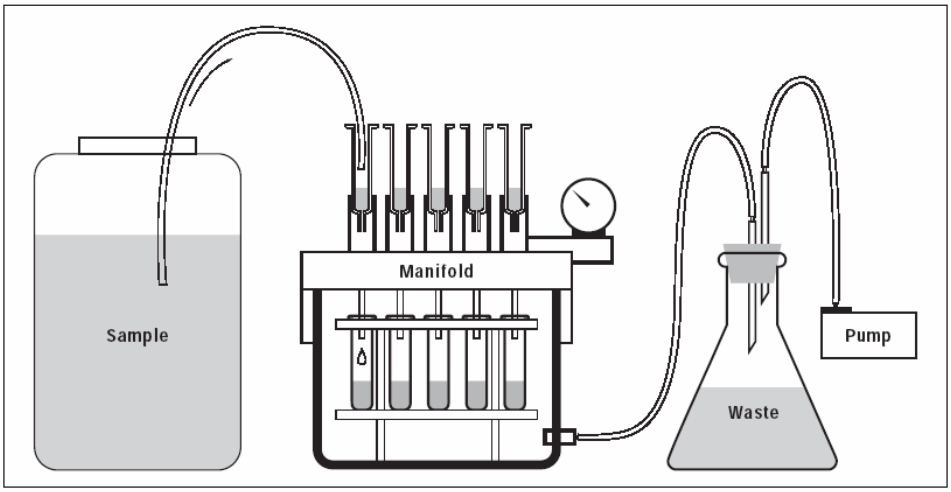

Figure 3.3 Schematic of apparatus for SPE using commercial cartridges

3.6.2 Ambersorb Solid-Phase Extraction (Amb SPE)

To establish an optimal Amb SPE procedure for NDMA extraction, several variables of the analytical method were examined including Ambersorb carbonaceous resin quantity, extraction time and salt addition. In these tests, all samples were prepared by spiking 10 µL of NDMA and NDMA-d_6 stock solutions into 500 mL of DI water (final 100 ng/L for either compound). After adding the internal standard, different amount of Ambersorb resins (100, 150 and 200 mg) were added to the samples. The samples were placed on a platform shaker at 175 rpm for 3 hours. The Ambersorb resins were collected by filtration and then extracted with 400 µL of methylene chloride. As shown in Figure 3.4, NDMA recovery increased with increasing quantify of Ambersorb resins that were used. To evaluate the effect of extraction time, samples were allowed for shaking for 1, 2, 3, and 4 hours, respectively, with 200 mg of Ambersorb resins. As shown in

Figure 3.5, extraction efficiency increased with longer extraction time; however, only slight increase in recovery was seen when exceeding 3 hours of extraction time.

Lastly, sodium chloride was added at 1, 2, and 4 M, respectively, to the water samples in the attempt to increase extraction efficiency. Studies have reported that extraction efficiency of NDMA could be improved by approximately 50% by the addition of up to 100 g/L of sodium chloride in the samples [Yoo et al., 2000]. Addition of inorganic salts has often been utilized to enhance the activity coefficients of organic compounds and thus lower solubility in aqueous solutions on the basis of the salting-out effect. The effect depends on the types of analyte and salt applied to the matrices [Schwarzenbach et al., 2002]. After salt addition, the samples were extracted for 3 hours with 200 mg Ambersorb resins. The extraction efficiency only slightly increased with NaCl addition as shown in Figure 3.6. Therefore, NaCl addition was not used for NDMA extraction in subsequent experiments based on the large amount of salt required and the modest increase in recovery.

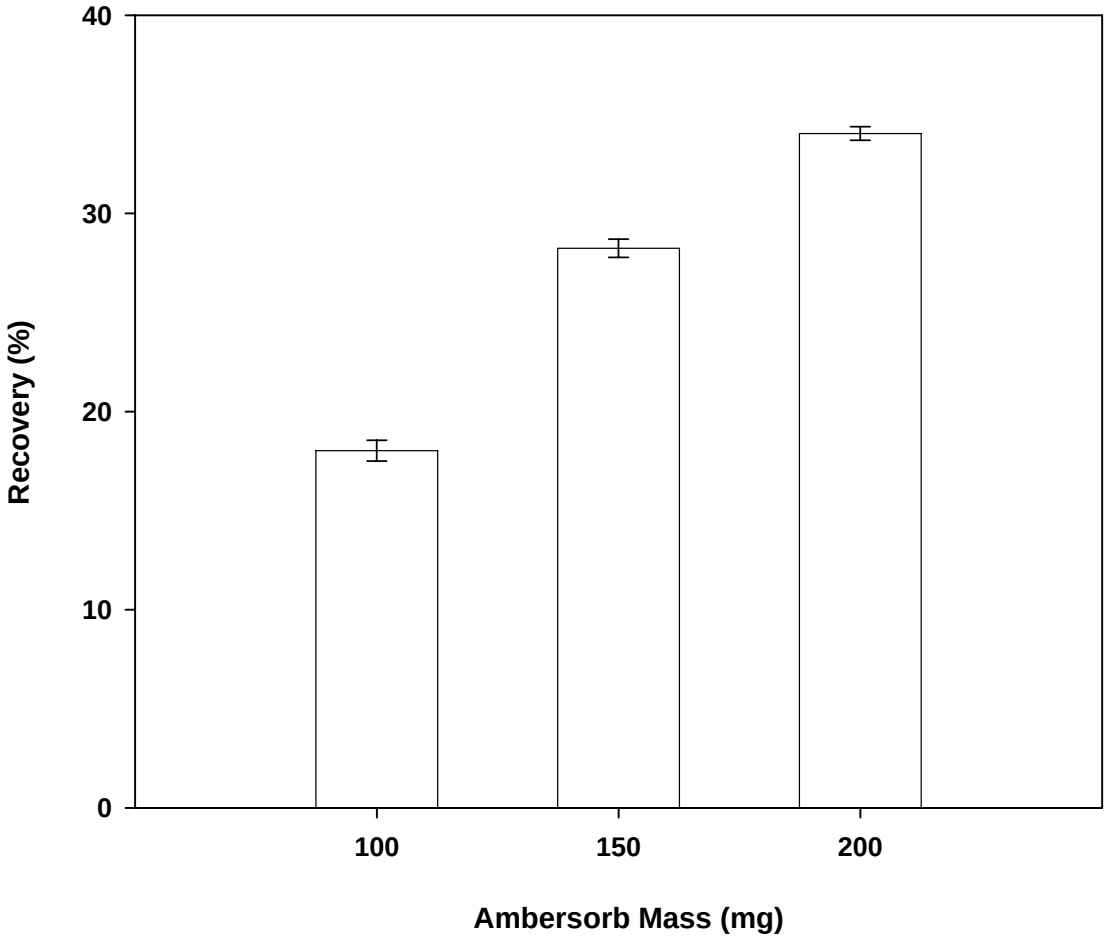

Figure 3.4 NDMA recovery vs. Ambersorb resin mass

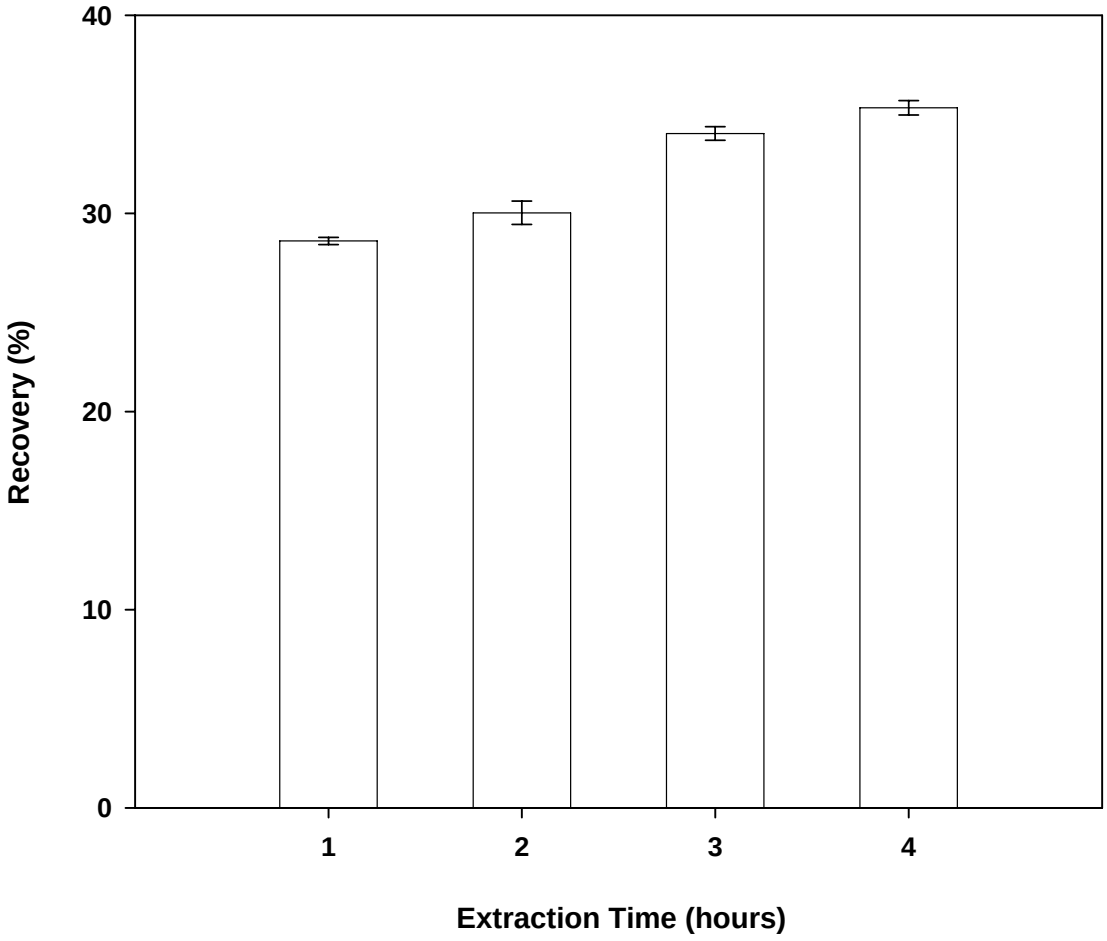

Figure 3.5 NDMA recovery vs. extraction time

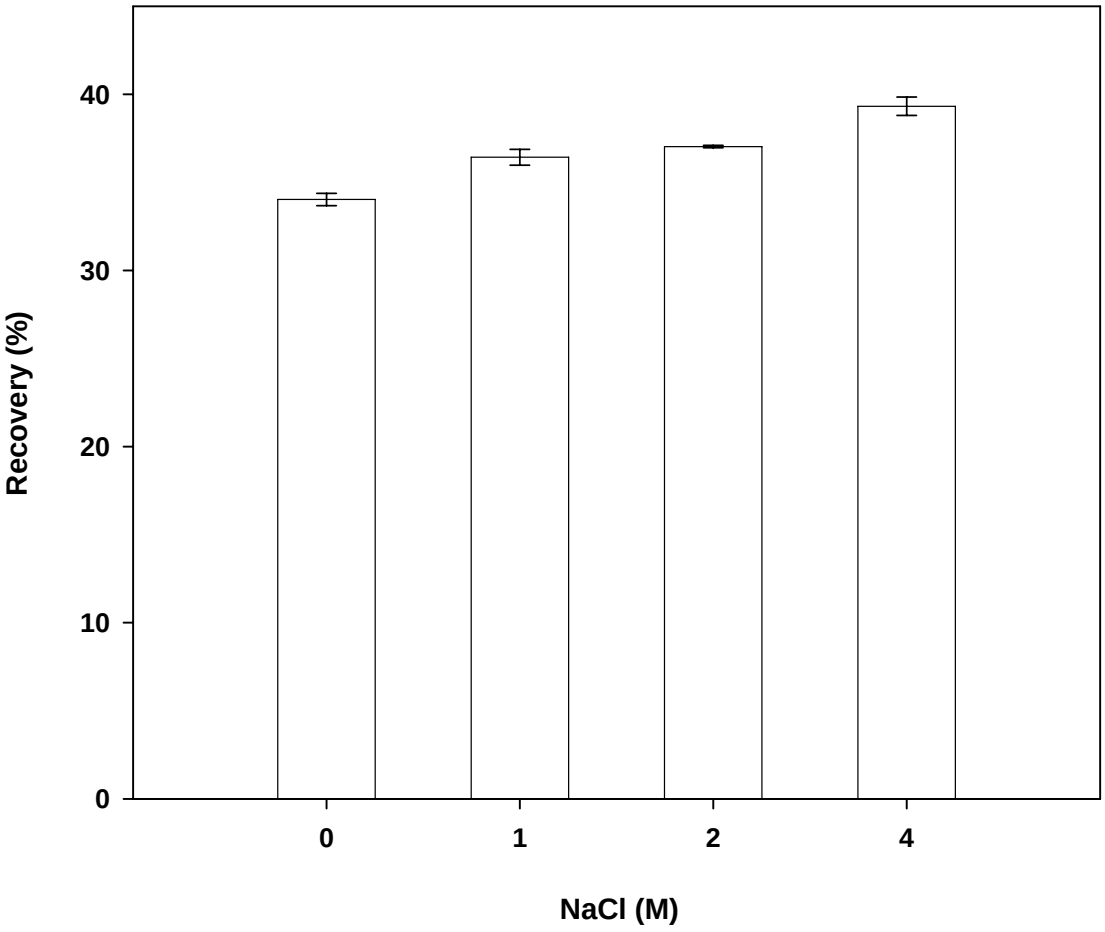

Figure 3.6 NDMA recovery vs. NaCl concentration

CHAPTER 4

Properties of the Water Treatment Polymers in Investigation

4.1 Polymers Investigated and Treatment Applications

Four types of polymers, cationic polyacrylamides (cationic PAMS), aminomethylated polyacrylamide (Mannich), poly-diallyldimethylammonium chloride (polyDADMAC) and polyamine, were investigated in this study. As shown in Figure 4.1, the cationic PAMS polymers are derived from the copolymerization of acrylamide with dimethylaminoethyl acrylate (DMAEA) in quaternized form. A first reaction of DMAEA with methyl chloride allows it to be converted into a quaternary ammonium salt in the form of chloromethylated DMAEA (DMAEA-MeCl). The copolymerization of DMAEA-MeCl with acrylamide produces the cationic copolymer. The cationic charge of the copolymer is determined by the ratio of each monomer and may vary between 0 and 100%. In addition, the ester group of the copolymer is very sensitive to pH and may hydrolyze at pH above 6.

The Mannich polymers are acrylamide homopolymers as shown in Figure 4.2. To prepare polyDADMAC, the DADMAC monomer is first obtained by the reaction of allyl chloride with dimethylamine (DMA). Polymerization of DADMAC via a cyclization mechanism forms the two possible structures of polyDADMAC (Figure 4.3). The quaternary polyamines are made from the condensation reaction of epichlorhydrin with a primary or secondary amine, usually DMA (Figure 4.4).

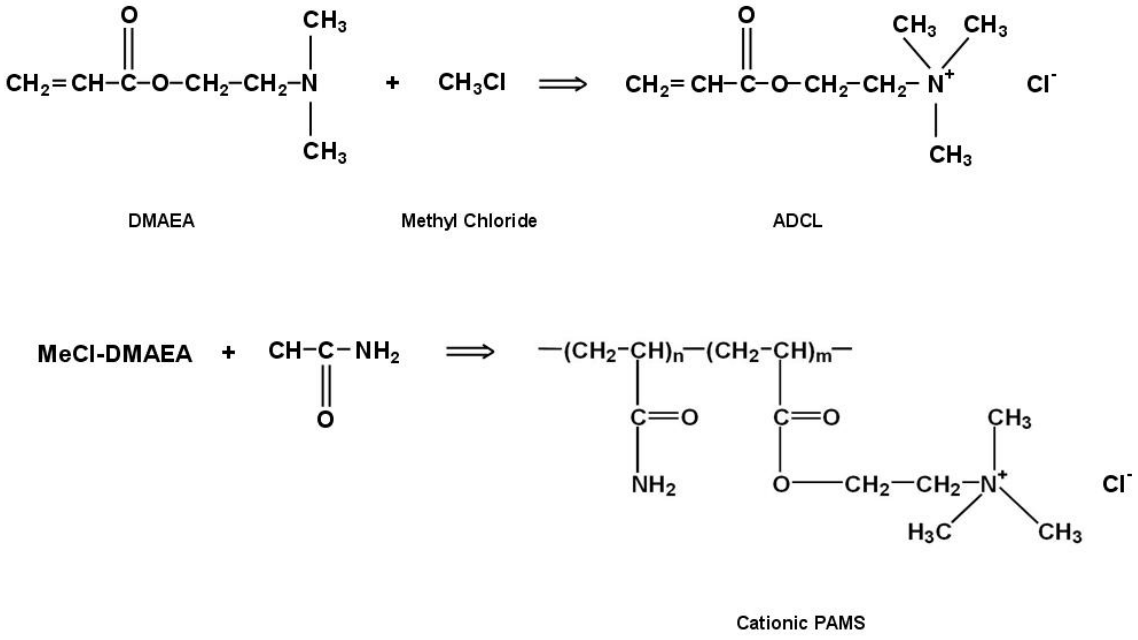

Figure 4.1 Synthesis of cationic PAMS co-polymer

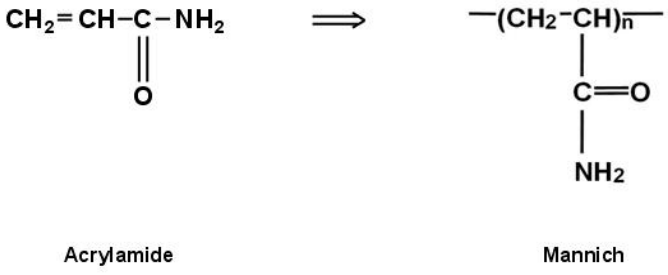

Figure 4.2 Synthesis of Mannich polymer

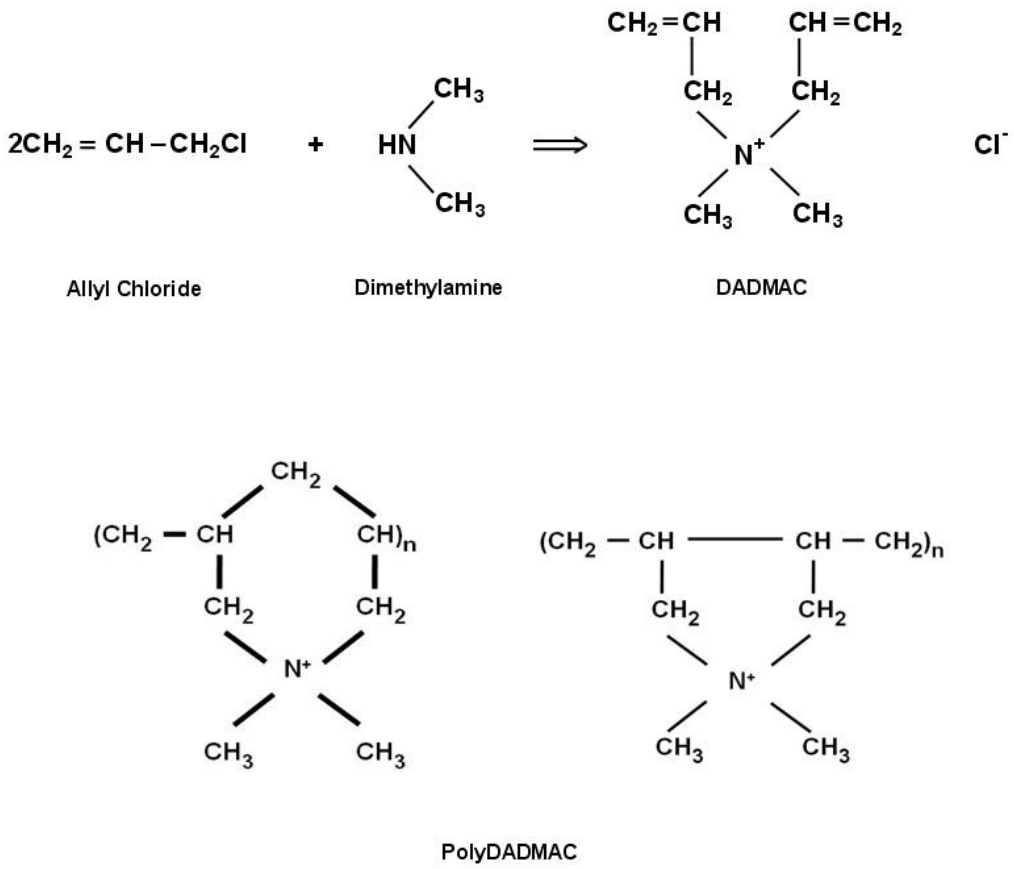

Figure 4.3 Synthesis of polyDADMAC

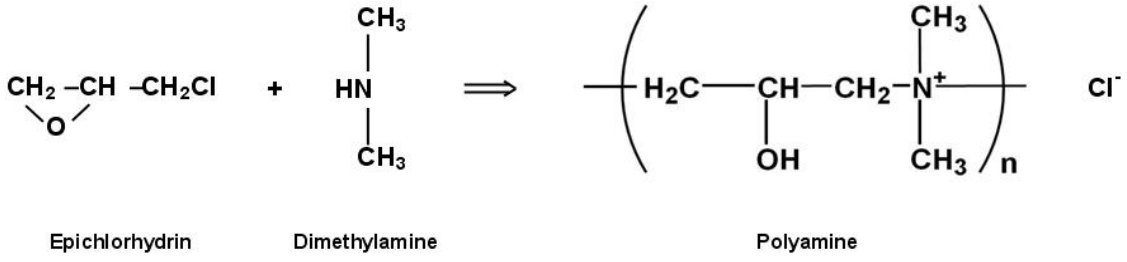

Figure 4.4 Synthesis of polyamine

Among these polymers, polyDADMAC and polyamine are typically used as coagulants in drinking water treatment. Cationic PAMS and nonionic Mannich polymers are used as flocculants in treatment of potable water and waste process water, as well as in sludge dewatering processes. The typical dosages of polymers in the above applications are about 0.3-1.5 mg/L in active ingredients [SNF, 2003]. Higher dosages of polymers are generally not used in real practice because they lead to poor coagulation and the problem of redispersion of polymer particles. The polymers also have very strong tendency to adsorb to particulates and the formed flocs in water. Therefore, the majority of the polymers applied are expected to be removed by sedimentation and filtration processes prior to disinfection processes. As a result, direct contact of the polymers with chlorine should be limited, except in cases where pre-oxidation is used prior to coagulation/flocculation processes, and for remaining polymers that are dissolved in water or bound to particulates that are not effectively removed by sedimentation and filtration. However, the time period of the above direct contact should also be taken into account for potential NDMA formation.

4.2 Properties of the Polymer Samples

All the polymers used in this study were obtained from the SNF Holding Company. The four polymer samples used in the reaction experiments were received in October, 2004, with the active ingredient contents listed below. The polymer samples were kept at room temperature (23 ºC) and protected from light in storage.

1) Powder grade cationic polyacrylamide polymer (80% cationic, 94.3% active)

2) Aminomethylated polyacrylamide solution polymer (Mannich) (4.39% active)

3) Poly-diallyldimethylammonium chloride (polyDADMAC) (40.3% active)

4) Polyamine solution polymer (49.7% active)

Note : 80% cationic means 80 Mole% cationic, which was prepared with 80 monomer units of DMAEA-MeCl to every 20 monomer units of acrylamide ; active means active ingredients (i.e., total non-volatile solids)

Other characteristics of the polymers were also determined by the SNF personnel and are summarized in Table 4.1.

Table 4.1 Characteristics of the polymer samples

	Cationic PAMS Powder	Mannich Solution Polymer	PolyDADMAC Solution Polymer	Polyamine Solution Polymer
Molecular Weight (dalton)	3 – 10 million	1.5 – 15 million	10,000 – 1 million	10,000 – 1 million
Viscosity (centipoises)	UL viscosity 4.26	31,750	2,880	840
pH	N.A.	10.5	6.0	5.9
Non-Volatile Solids	94.3%	4.39%	40.3%	49.7%
Residues	Residual acrylamide 35 ppm	N.A.	Residual monomer < 0.1%	Epi = 0 ppm Glycidol = 0 ppm DCIPA = 236 ppm DCPA = 78 ppm DIOL = 34 ppm TOC = 347 ppm

Note: N.A. = not available; Epi = Epichlorhydrin; DCIPA = 1,3-dichloro-2-propanol; DCPA = 2,3-dichloro-1-propanol; DIOL = 3-chloro-1,2-propanediol and TOC = Total Organic Content.

4.3 Concentrations of DMA and NDMA in the Polymer Solutions

As discussed in the previous section that DMA is used as s starting material in the synthesis of some of the polymers, therefore the presence of residual DMA and NDMA contaminants is possible in the polymer samples and needs to be determined. In these experiments, 10 mg of each polymer stock were dissolved in 1-L DI water that was buffered at pH 7.5 using 10 mM phosphate buffer. The resulting active polymer concentrations were 9.43, 0.44, 4.03 and 4.97 mg/L for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively. The samples were kept in 1-L amber glass bottle with almost no headspace. DMA and NDMA concentrations were analyzed within 4 hours of sample preparation (i.e., representing freshly prepared polymer solutions) using the procedures described in Chapter 3. DMA and NDMA concentrations were also examined after 10, 20, 45, and 70 days for the purpose to evaluate the stability of DMA in the diluted polymer solutions and potential NDMA formation just from the polymers alone. Duplicate samples were prepared and analyzed in each case. The average number and associated standard deviation were reported.

For all of the samples, the concentrations of NDMA ranged from 10 to 59 ng/L, close or below to the detection limits of NDMA in the polymer solution matrices. There was also no apparent increase or decrease of NDMA concentration over the time span of 4 hours to 70 days.

On the contrary, measurable DMA was detected in the samples. The concentrations of DMA measured in the freshly prepared polymers solutions are shown in Table 4.2. These concentrations were divided by the corresponding active concentration of the polymer to obtain the background DMA contained in each polymer

(in μg DMA per mg polymer). Analyses indicated that the Mannich polymer contained a very large amount of DMA while the other polymers contained relatively small amounts of DMA (Table 4.2), with cationic PAMS contained the lowest amount of DMA. Analyses also showed that DMA concentrations decreased significantly with increasing storage times. The DMA concentration decreased to below 2 μg/L in cationic PAMS, polyDADMAC and polyamine after 70 days. Even for Mannich, the DMA concentration decreased to near 15 μg/L after 70 days. The specific reasons for the DMA loss are not clear currently. Slow volatilization of DMA over time might be a reason.

Table 4.2 Measured DMA concentrations in fresh polymer samples at pH 7.5, 23ºC.

Polymer Type	Active Polymer Conc. (mg/L)	Measured DMA Conc. (μg/L)	Background DMA in the polymer (μg/mg)
Cationic PAMS	9.47	3.87	0.41
Mannich	0.44	3462 ± 110	> 7800 ± 250
PolyDADMAC	4.03	14.72 ± 0.35	3.65 ± 0.09
Polyamine	4.97	28.14 ± 6.38	5.67 ± 1.28

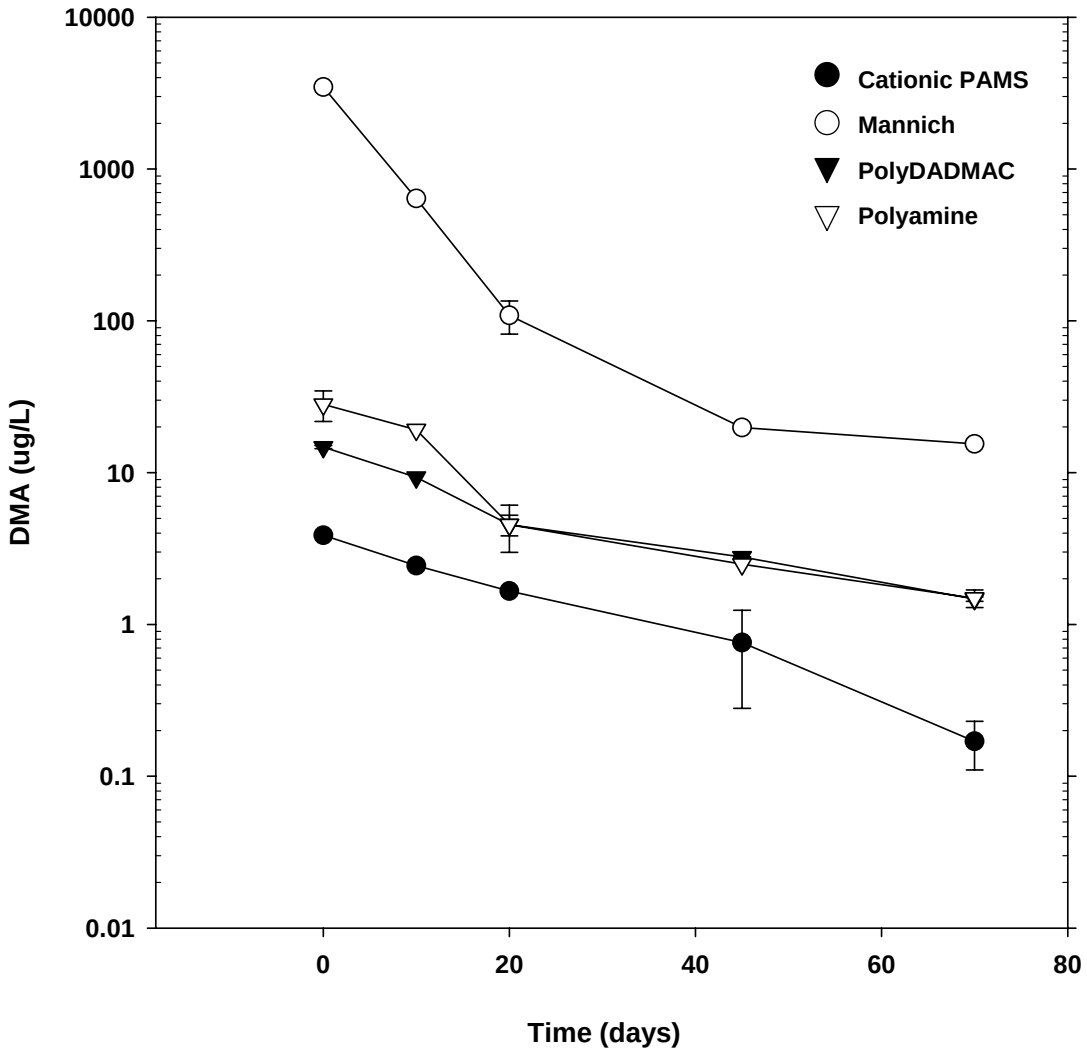

Figure 4.5 Decrease of DMA concentrations in polymer solutions at pH 7.5 (10mM phosphate buffer), 23 °C over time. Polymer concentrations: 9.43, 0.44, 4.03 and 4.97 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

Similar analyses were conducted again but with lower concentrations of polymers and at pH 8.5. DMA concentrations were measured in the freshly prepared polymer solutions and after 7 days as shown in Table 4.3. The measured DMA concentrations (per mg of polymer) at pH 8.5 were slightly lower than those measured at pH 7.5. At both pH 7.5 and 8.5, the majority of DMA (pK_a = 10.73) is protonated in the solution with only a small fraction present in the neutral form (i.e., the species that is susceptible to volatization). Therefore, significant volatization of DMA is not expected in the system. However, the fraction of the neutral form species is greater at the higher pH. Thus, this might cause the lower amount of DMA detected in the polymer solutions. This difference might be caused by a greater extent of DMA volatilization at the higher pH.

Table 4.3 Measured DMA concentrations in polymer samples at pH 8.5, 23ºC.

Polymer Type	Active Polymer Conc. (mg/L)	Measured DMA Conc. (µg/L) in fresh polymer	Measured DMA Conc. (µg/L) after 7 days	Background DMA in fresh polymer (µg/mg)
Cationic PAMS	4.74	0.70 ± 0.21	0.81 ± 0.01	0.18 ± 0.04
Mannich	0.22	1293 ± 50	97.9 ± 4.9	> 5800 ± 227
PolyDADMAC	2.02	5.71 ± 1.13	10.73 ± 1.49	2.83 ± 0.56
Polyamine	2.49	4.10 ± 0.34	6.72 ± 0.94	1.65 ± 0.14

CHAPTER 5

Potential NDMA Formation from Water Treatment Polymers

5.1 Screening Polymers for NDMA Formation Potential

As an initial phase in a multi-year project, an important objective of this study was to screen various water treatment polymers for potential NDMA formation. For this purpose, high dosage of polymer and disinfection oxidant was employed in order to assess the maximum potential of polymers to yield NDMA, rather than to simulate the actual water treatment processes. Each of the four water treatment polymers (cationic PAMS, Mannich, polyDADMAC and polyamine) was evaluated for potential NDMA formation upon exposure to nitrite, monochloramine, free chlorine or chlorine dioxide oxidants, respectively. The typical employed polymer concentrations were 23.58, 0.88, 20 and 9.94 mg/L active, for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively, higher than the typical 0.3-1.5 mg/L active polymer dosage in drinking water and wastewater treatment plants. The employed oxidant concentrations were listed as six different conditions below, also comparable or higher than the typical chlorine dosages in treatment plants (typically 1-5 mg/L in potable water treatment and 5-10 mg/L in wastewater treatment:

(1) NO_2^- 20 mg/L

(2) HOCl 10 mg/L as Cl_2

(3) NH_2Cl 10 mg/L as Cl_2

(4) ClO_2 8 mg/L as Cl_2

(5) ClO_2 8 mg/L as Cl_2 plus NO_2^- 20 mg/L

(6) ClO_2 8 mg/L as Cl_2 plus DMA 0.3 mM

Reactions of polymers and oxidants were conducted in 1-L amber glass batch reactors to prevent UV light from reaching the samples. Duplicate samples were prepared for each condition investigated. Instrument blank and Ambersorb resin blank were analyzed to ensure no background contamination in the instrument or resins. Blank controls (polymer alone in the given matrix) and matrix controls (oxidant alone in the given matrix) were also evaluated for each set of experiments. Polymer, pH buffer and oxidant stock solutions were prepared freshly and used within 4 hours. Reactions were conducted at pH 7 with 4-10 mM phosphate buffer concentrations. The pH was monitored at the beginning and the end of each reaction, and never shifted more than 0.5 pH unit. Buffer solution was added first to 500-800 mL water sample, followed by polymer solution and lastly the oxidant. The sample reactors were kept in the dark and at room temperature (23 ± 2 ºC) during the reaction. After 24 hours of reaction time, excess ascorbic acid (20 mg/L) was added to quench the remaining oxidant (chlorine, monochloramine or chlorine dioxide) and stop the reaction. This quenching method was not used for the reactions with nitrite. After quenching, the internal standard isotope NDMA-d_6 was then spiked into the sample just prior to NDMA extraction following the procedures described in Chapter 3. For DMA analysis, 100 mL of the sample was separated, spiked with the internal standard DMA-d_6 and analyzed for DMA following the procedures described in Chapter 3. The results of the duplicate experiments were averaged and reported with the associated standard deviation.

The reaction experiments were conducted in DI water matrix as well as in real wastewater matrix to evaluate the impact of wastewater constituents on the NDMA formation potential of the polymers. The wastewater sample used in the experiments was

collected from the RM Clayton Wastewater Treatment Plant near Atlanta, GA, a primarily domestic wastewater treatment plant at the capacity of 120 millions of gallons per day (MGD). The wastewater samples were collected at the point after the processes of activated sludge and the secondary clarifier. Upon immediately brought back to the laboratory, the wastewater was filtered by glass fiber filters to remove larger particles. The characteristics of the filtered wastewater were determined to be: pH = 6.93, total organic carbon (TOC) = 5.4 mg/L and total suspended solids (TSS) = 1.3 mg/L according to the Standard Methods [APHA, 1998]. The wastewater samples were kept at 4 ºC in dark and used within a week.

As will be shown later, the screening experiments indicated that reaction with monochloramine yielded the highest amount of NDMA. Therefore additional studies were conducted to assess several common parameters that were expected to have significant impact on the NDMA formation upon chloramination of water treatment polymers. The parameters included polymer dosage, monochloramine dosage, contact time, and the effect of sequential addition of free chlorine and ammonia.

5.2 Results and Discussion

5.2.1 Screening Results

The results obtained from the blank controls (i.e., polymers alone without oxidants) showed that the polymer solutions (0.8-23.58 mg/L active) contained 20 ± 1 ng/L or less NDMA (Data are shown in the Appendix Table A.1). Based on the typical polymer dosages (0.3-1.5 mg/L) in most water treatment plants, these polymers themselves are unlikely significant sources of NDMA. No detectable amount (< 15 ng/L)

of NDMA was found in the DI water alone or in the DI water matrix control experiments (Table A.1 in the Appendix).

When the polymers were in contact with each of the four oxidants, significant amount of NDMA was generated in some cases. Because different concentrations of polymers were used in the experiments, the measured NDMA concentration was divided by the corresponding polymer concentration (yielding NDMA concentration in ng NDMA per mg polymer unit) to aid comparisons among the four polymers. The results for reactions with nitrite, free chlorine, monochloramine (preformed) and chlorine dioxide are shown in Figures 5.1-5.4. Numerical data are also available in the Appendix Table A.1.

Overall, reactions with monochloramine (Figure 5.3) yielded significantly higher levels of NDMA than reactions with nitrite, free chlorine, or chlorine dioxide. Reactions with free chlorine generated relatively low levels of NDMA with the highest NDMA concentration observed with the Mannich and polyamine polymers (Figure 5.2). Reaction with chlorine dioxide yielded the lowest levels of NDMA, with the highest NDMA concentration also seen with the Mannich polymer (Figure 5.4). Reactions with nitrite (Figure 5.1) yielded significant levels of NDMA especially for the Mannich polymer; however, the employed nitrite concentration was much higher than what would be seen at typical treatment plants. The significance of these results is demonstration of the possibility of NDMA formation from the polymers under nitrosation conditions.

Among the four polymers, the cationic PAMS yielded the least amount of NDMA when reacted with the oxidants. The Mannich polymer yielded the highest levels of NDMA in reactions with the oxidants, with exceptionally high NDMA yield in reaction

with monochloramine. The polyDADMAC and polyamine polymers yielded comparable levels of NDMA with the polyamine polymer sometimes generating slightly higher levels of NDMA than the polyDADMAC polymer. As shown in Tables 4.1 and 4.2, the lowest concentration of DMA was found in the cationic PAMS polymer sample, and the highest concentration of DMA was found in the Mannich polymer sample. The concentrations of DMA in polyDADMAC and polyamine were comparable. Thus, the NDMA formation potentials observed in the screening experiments seem to be consistent with the trend of DMA precursor levels present in the polymers.

In addition, a slightly higher level of NDMA formation was generally observed in wastewater matrix compared to that in DI water matrix. This is also consistent with expectation since wastewater matrix contains other constituents such as natural organic matter that may also behave as NDMA precursors in the sample, adding to the overall amount of NDMA formed.

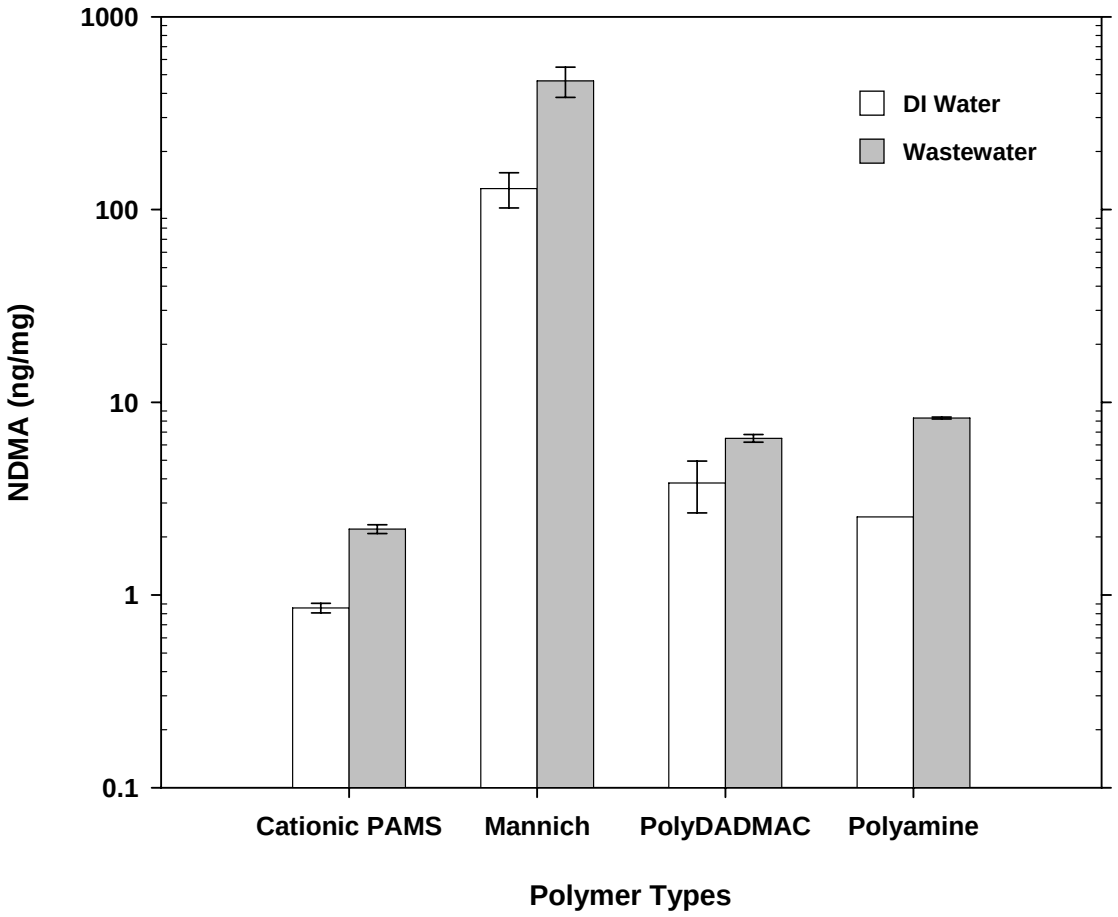

Figure 5.1 NDMA formation after 24 h reaction. NO_2^- (20 mg/L) was added to polymer solutions (0.8 – 23.6 mg/L active). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

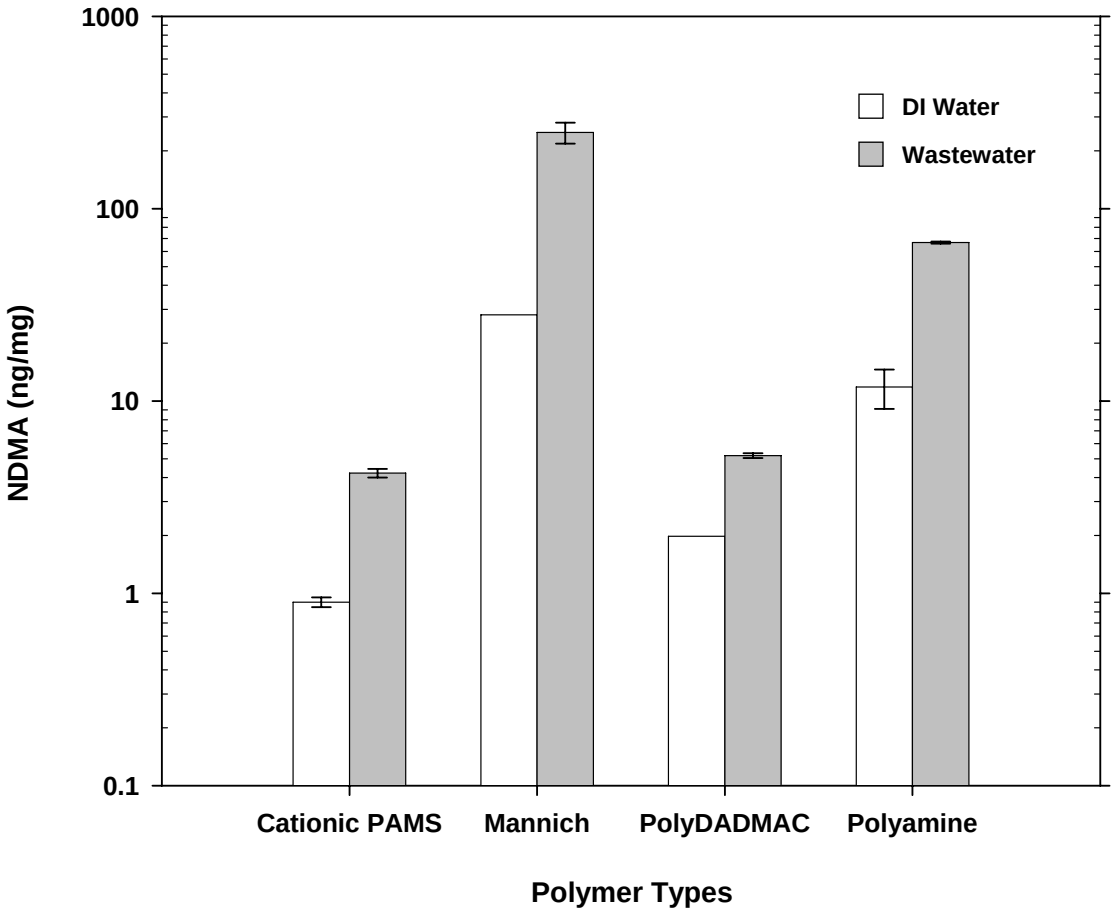

Figure 5.2 NDMA formation after 24 h reaction. HOCl (10 mg/L as Cl_2) was added to polymer solutions (0.8 – 23.6 mg/L active). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

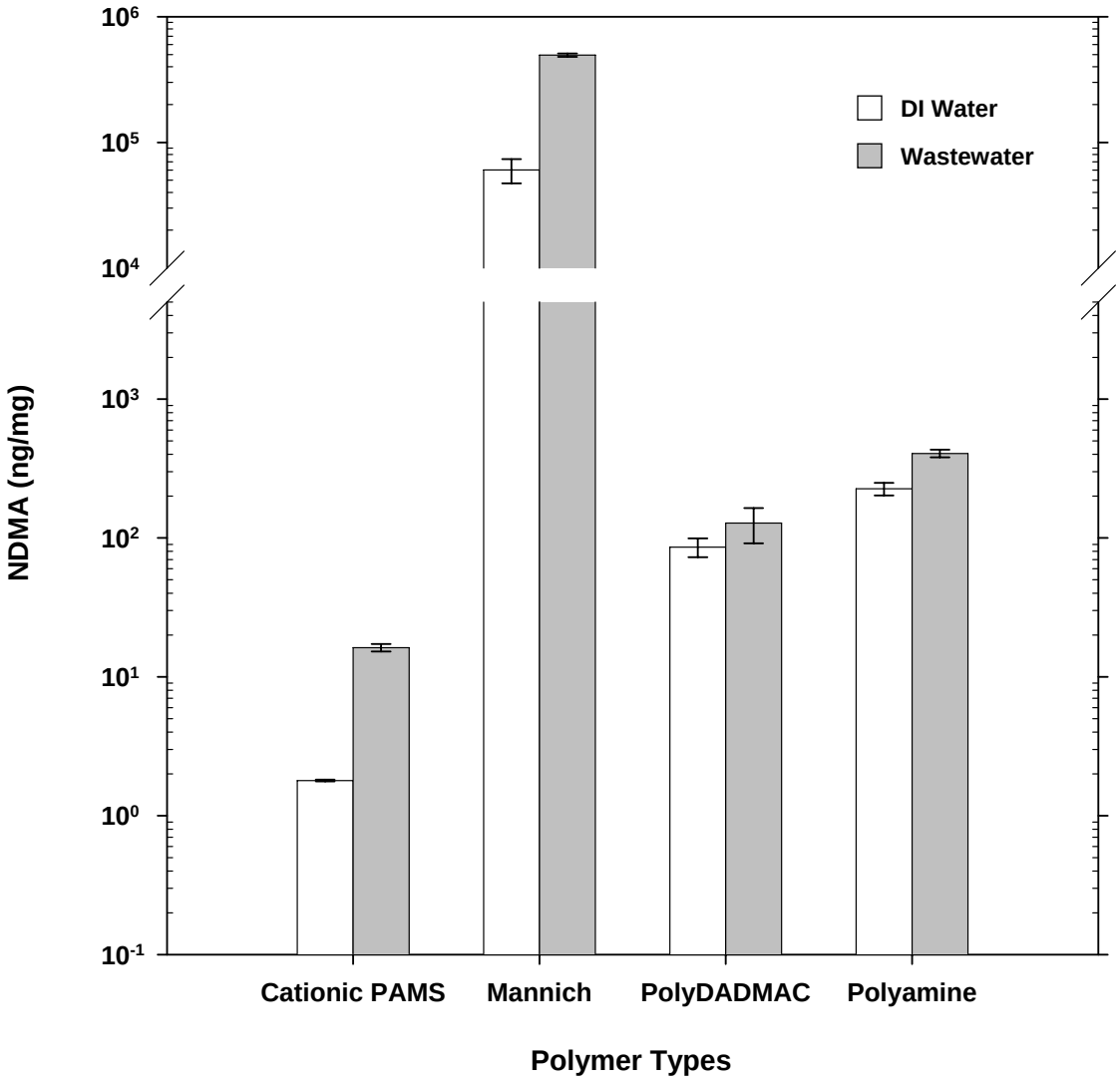

Figure 5.3 NDMA formation after 24 h reaction. NH_2Cl (10 mg/L as Cl_2) was added to polymer solutions (0.8 – 23.6 mg/L active). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

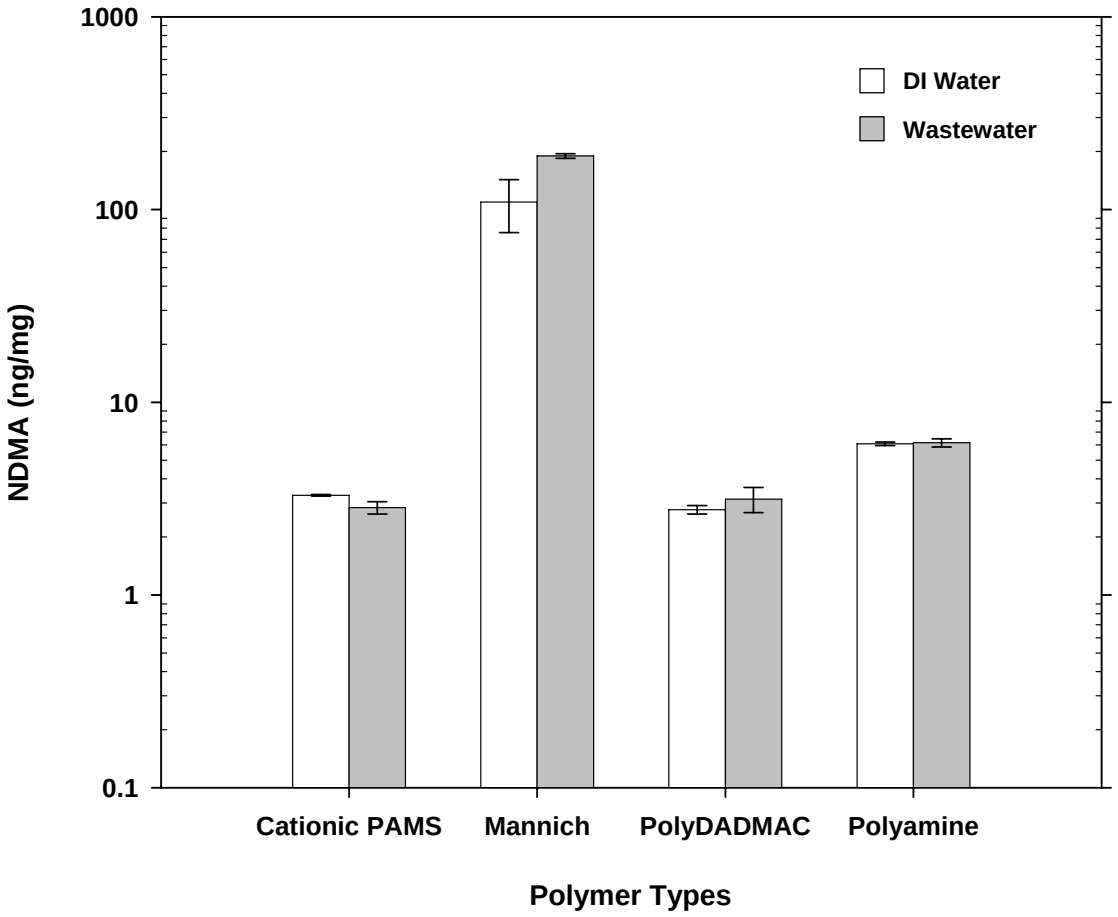

Figure 5.4 NDMA formation after 24 h reaction. ClO_2 (8 mg/L as Cl_2) was added to polymer solutions (0.8 – 23.6 mg/L active). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

The reactions between the polymers and chlorine dioxide were also investigated under the conditions with additional amendment of nitrite and DMA, respectively (Figures 5.5 and 5.6, Appendix Table A.1). In these experiments, nitrite or DMA was added to the water sample shortly after the polymer addition and immediately before the chlorine dioxide addition. The purpose of these experiments was to assess whether nitrite and DMA might enhance polymer NDMA formation potential in reactions with chlorine dioxide.

In the matrix control experiments, it was found that the reaction between DMA and ClO_2 and the reaction between nitrite and ClO_2 did not generate significant level of NDMA (< 15 ng/L). When DMA was added to the reaction of polymers with chlorine dioxide, only slight increase in NDMA yields was observed (Figure 5.6) compared to those without DMA addition (Figure 5.4). In contrast, a significant increase in NDMA formation was observed when adding nitrite to the reactions of polymers and chlorine dioxide (Figure 5.5). The increase was significant in the Mannich, polyDADMAC and polyamine polymers. In each case, the generated NDMA level was considerably higher than the sum of NDMA formation from adding either chlorine dioxide or nitrite alone. In addition, the levels of NDMA formed were found to be lower in the wastewater matrix than in the DI water matrix (Figure 5.5), in contrast to the other experiments. Currently the reasons for these observed phenomena are not clear and further studies are necessary.

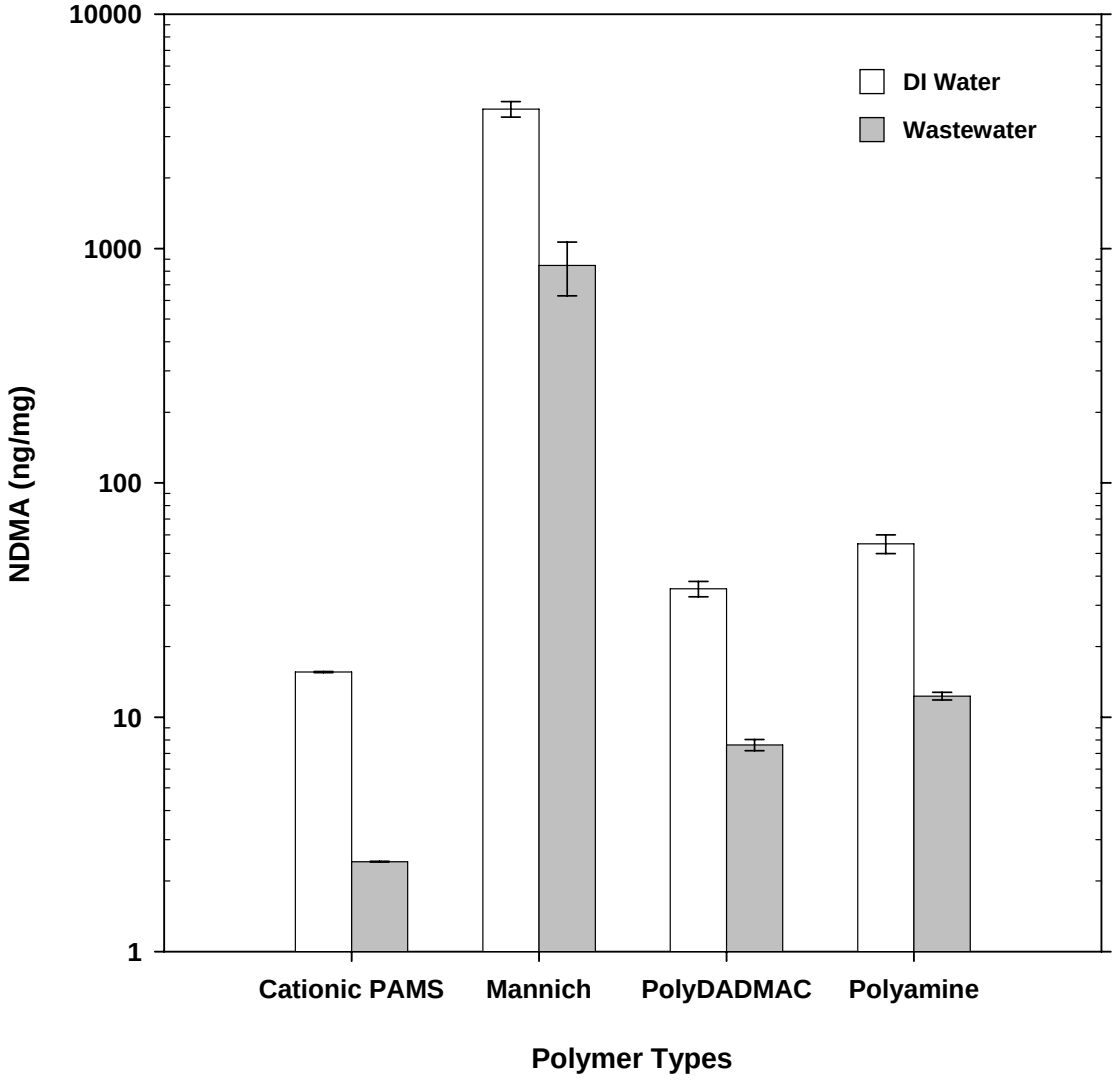

Figure 5.5 NDMA formation after 24 h reaction. NO_2^- (20 mg/L) was added to polymer solutions (0.8 – 23.6 mg/L active) prior to adding ClO_2 (8 mg/L as Cl_2). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

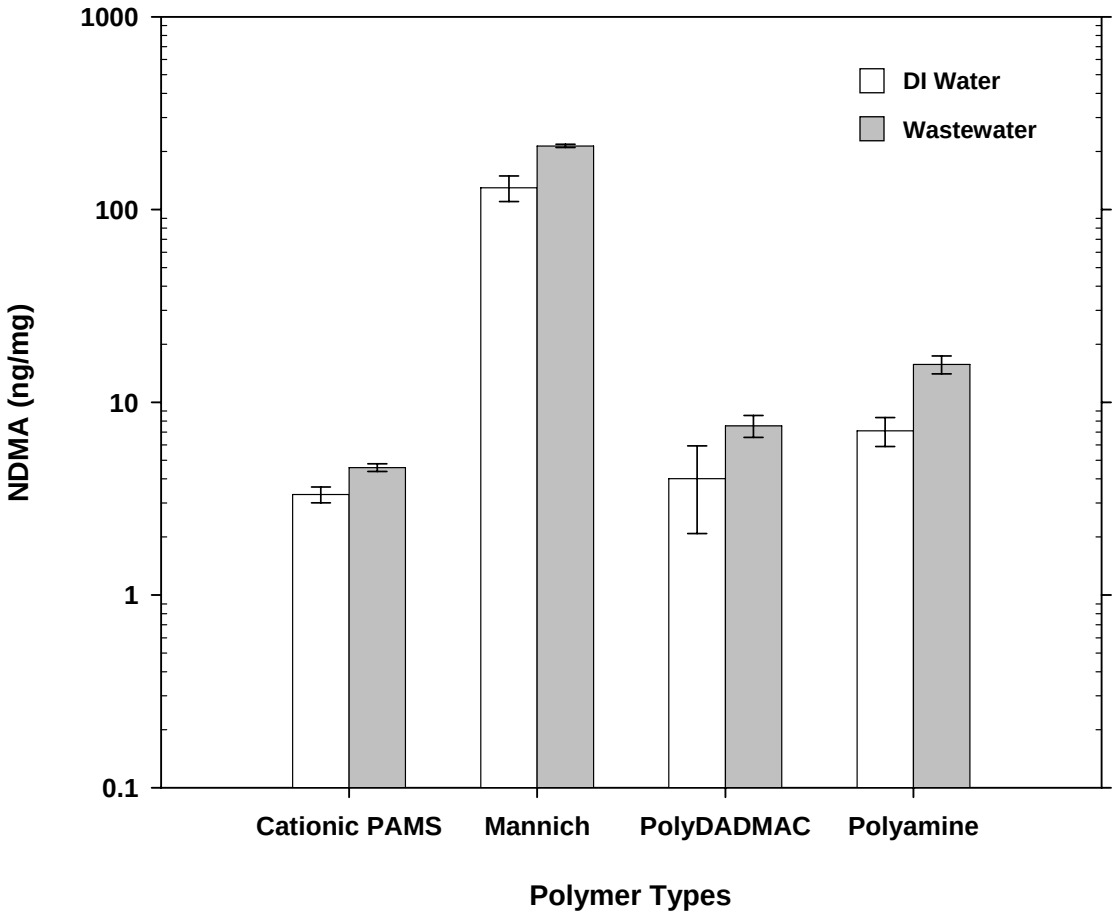

Figure 5.6 NDMA formation after 24 h reaction. DMA (0.3 mM) was added to polymer solutions (0.8 – 23.6 mg/L active) prior to adding ClO_2 (8 mg/L as Cl_2). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. T = 23 °C.

5.2.2 Impact of Polymer Dosage

To evaluate the effect of polymer dosage on the formation of NDMA during monochloramination, three polymer dosages were tested for each polymer (original concentration and 2 and 4 times of the original concentrations) upon exposure to the same dosage of monochloramine (4 mg/L as Cl_2). After seven days of reaction time, the samples were quenched and analyzed for NDMA and DMA concentrations. The residual monochloramine was found to be in the range of 2.3 to 2.8 mg/L (as Cl_2) after the reaction.

As shown in Figure 5.7, although the total molar concentration of NDMA increased with increasing polymer dosage, the polymer weight averaged NDMA yield (i.e., μg NDMA per mg polymer) actually decreased slightly with increasing polymer dosages. This decrease was more obvious for the cationic PAMS, polyDADMAC and polyamine polymers than for the Mannich polymer.

The molar concentrations of DMA measured after reactions from different dosages of polymers are shown in Figure 5.8. In general, the DMA concentration was higher with higher dosage of polymer in use. However, the relationships between the DMA concentration (after chloramination) and the initial polymer concentration were not linear except for the Mannich polymer. It is also important to point out that, compared to the original DMA concentration present in the polymer solution (after 7 days) without exposure to monochloramine (Table 4.2), higher DMA concentration was found after exposure to monochloramine for all of the four polymers. These results seem to imply that reactions of the polymers with monochloramine lead to release of more DMA from the polymers.

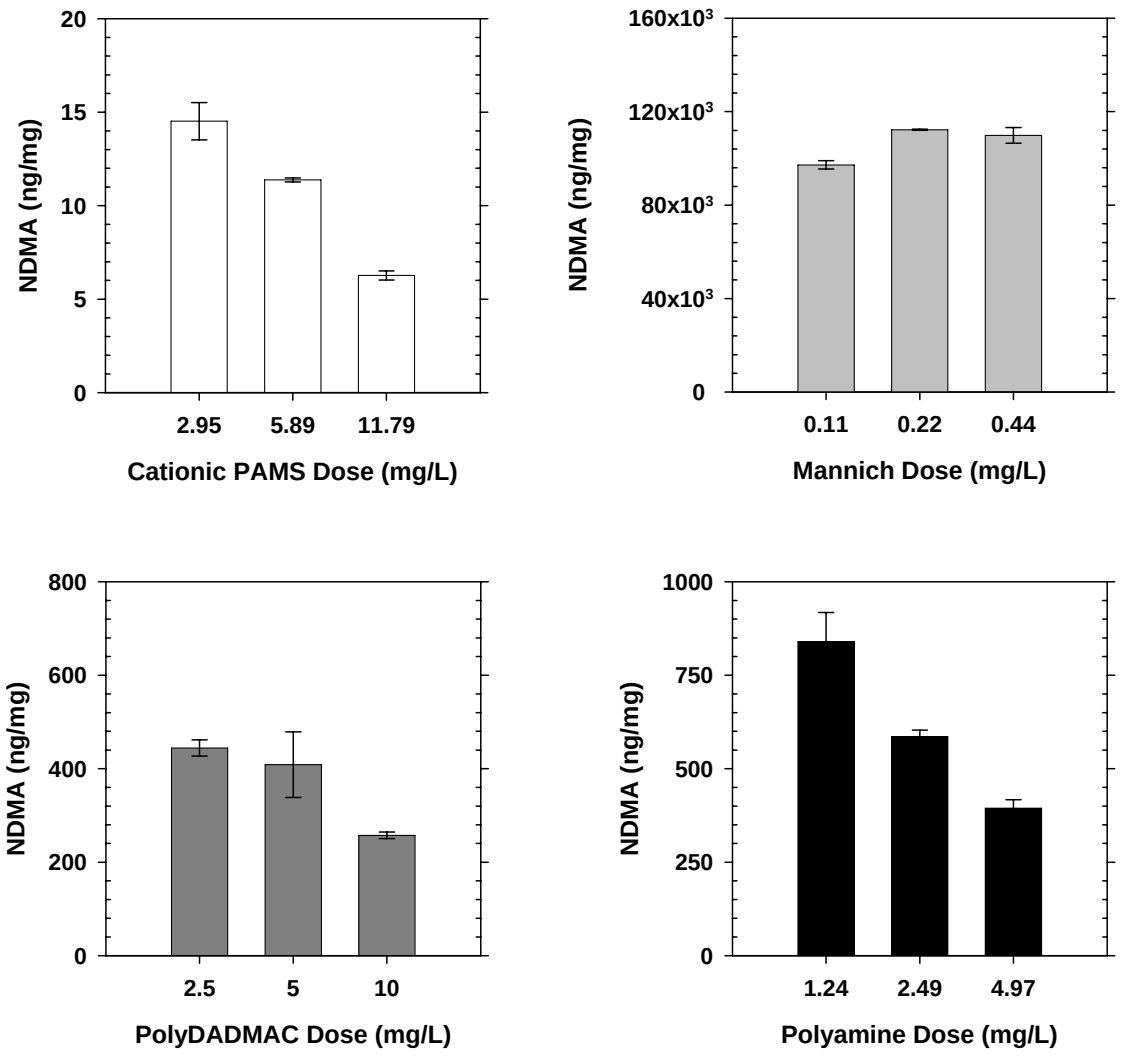

Figure 5.7 Effect of polymer dosage on NDMA formation. Reaction conditions: initial $[NH_2Cl]$ = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC.

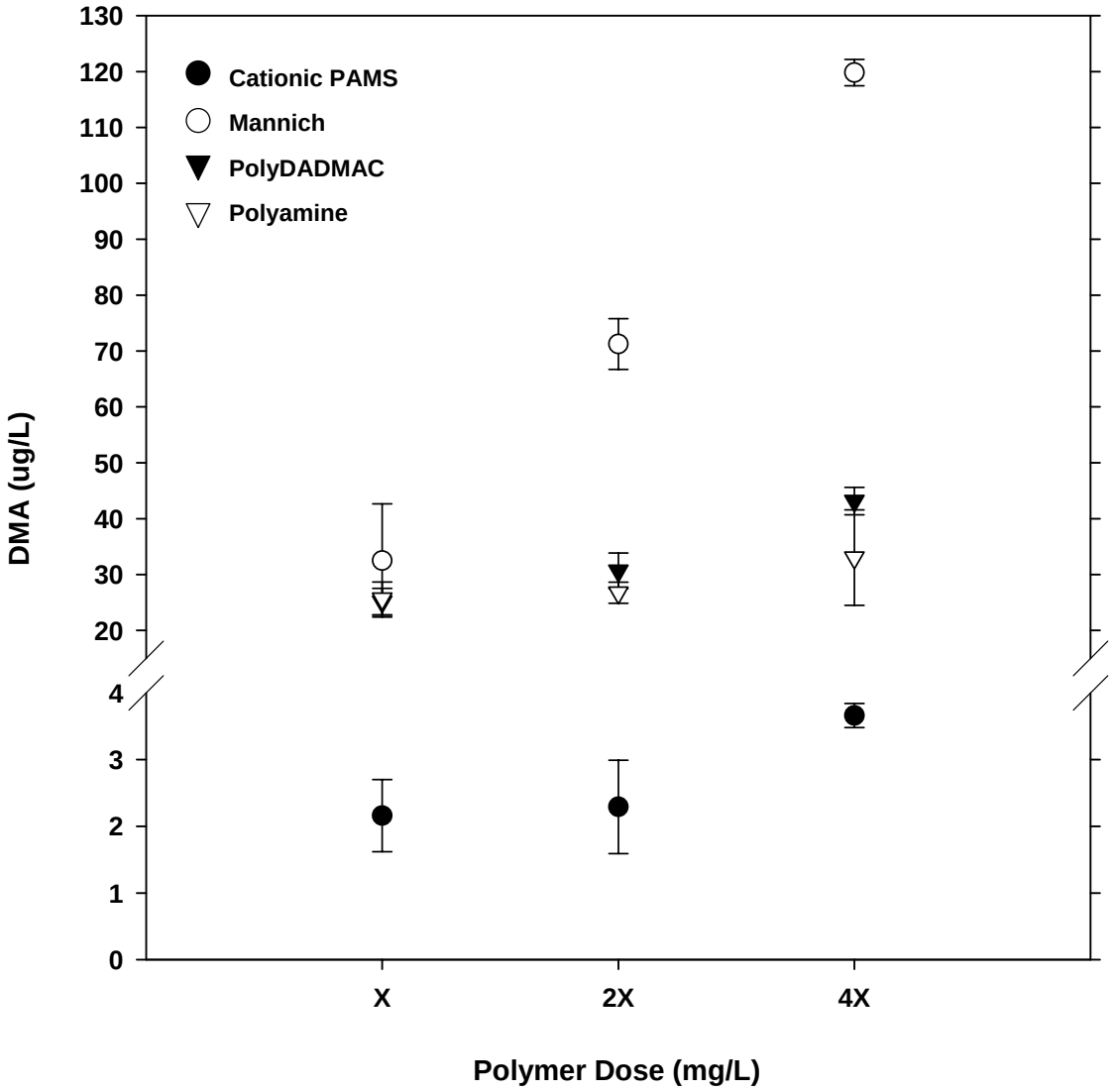

Figure 5.8 Relationship of DMA concentration and polymer dosage after reaction with monochloramine. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer dosage x = 2.95, 0.11, 2.5 and 1.24 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

5.2.3 Impact of Monochloramine Contact Time

To evaluate the effect of monochloramine contact time on the NDMA formation, each of the polymer was allowed to react with monochloramine (4 mg/L as Cl_2) for the period of 2, 4, and 7 days, respectively. At the end of the reaction, samples were quenched and concentrations of NDMA and DMA were analyzed as shown in Figures 5.9 and 5.10. The NDMA yield increased slightly with extended monochloramine contact time with the exception of the Mannich polymer, which did not have increase in NDMA yield. Noticeable increase in the DMA concentration was observed for the Mannich polymer, particularly after 7 days of monochloramine contact time. The DMA concentration only increased slightly with increasing monochloramine contact time for the cationic PAMS, polyDADMAC and polyamine polymers. The residual monochloramine in these tests was in the range of 2.1 to 2.8 mg/L (as Cl_2) after the reaction.

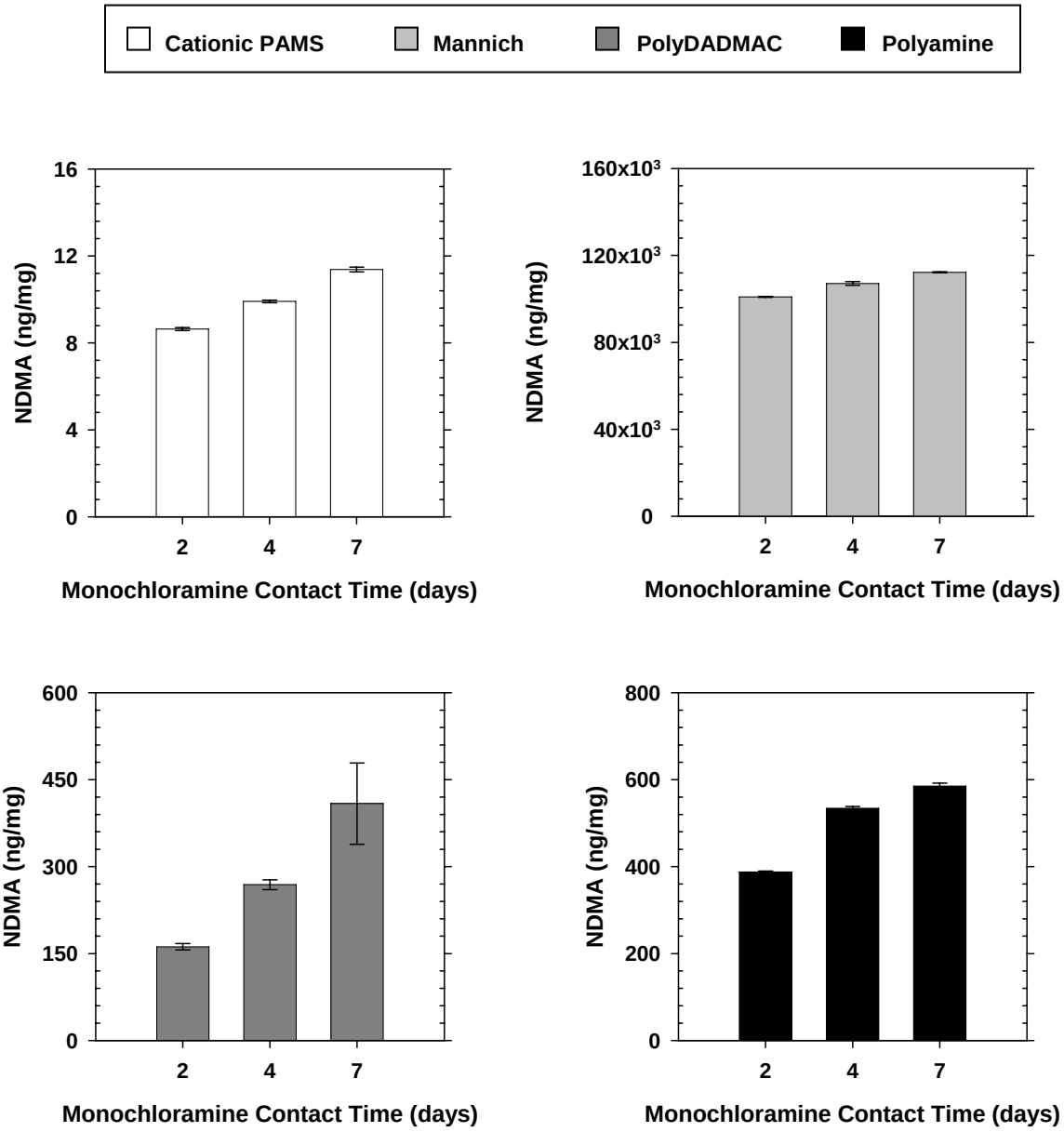

Figure 5.9 Effect of monochloramine contact time on NDMA formation. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

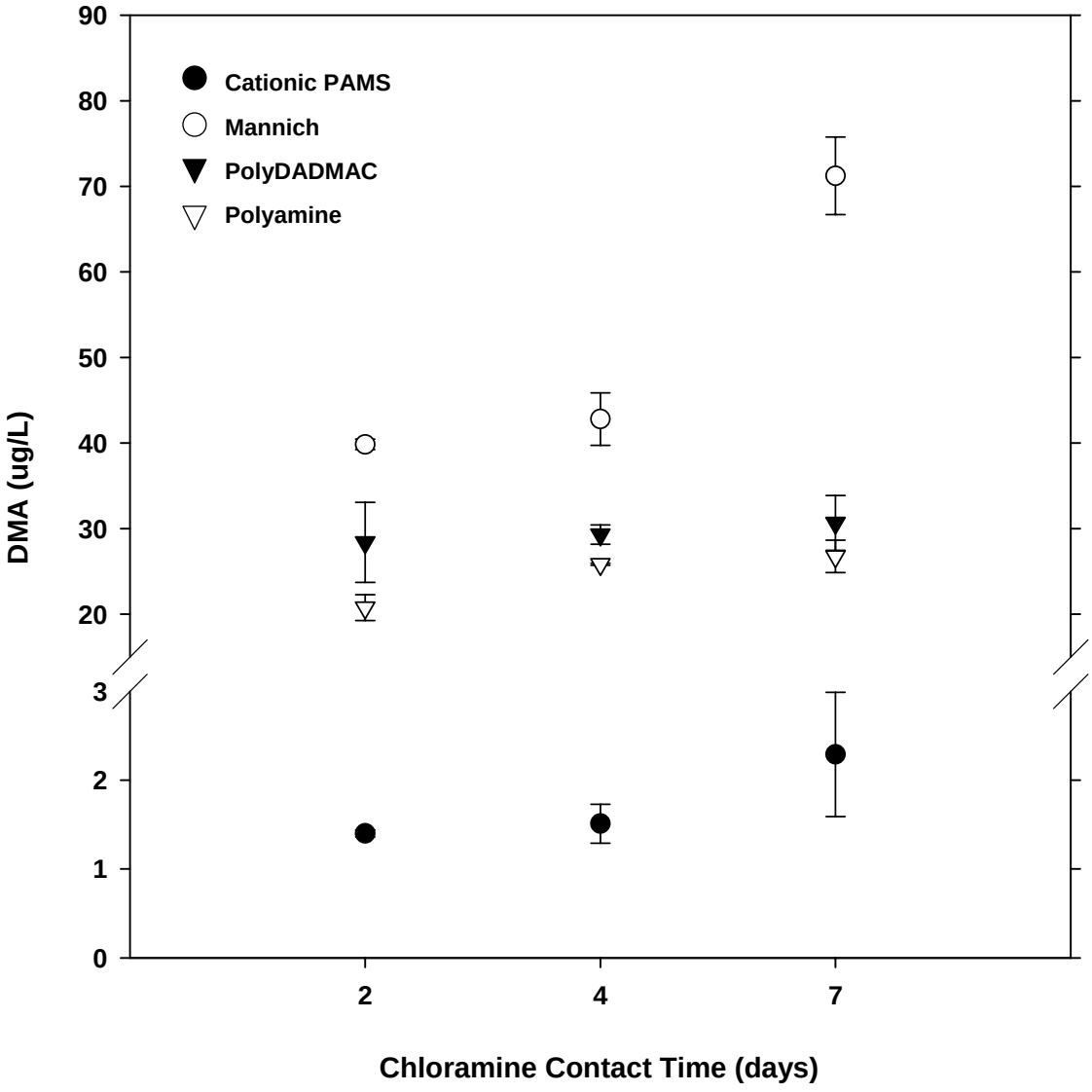

Figure 5.10 DMA concentration as a function of time. Reaction conditions: initial $[NH_2Cl]$ = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

5.2.4 Impact of Monochloramine Dosage

The polymers were exposed to two different monochloramine concentrations (4 and 8 mg/L as Cl_2) for the same period of 7 days to evaluate the impact of monochloramine dosage on resulting NDMA yield and DMA concentration. As shown in Tables 5.1 and 5.2, both NDMA yield and DMA concentration were higher with the higher monochloramine dosage. The residual monochloramine in the low and high oxidant concentration tests was 2.2 and 5.4 mg/L (as Cl_2), respectively, after the reaction.

Table 5.1 Effect of monochloramine dosage on NDMA formation from the polymers. Reaction conditions: initial [NH_2Cl] = 4 and 8 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	NDMA Yield (ng/mg polymer)	
	[NH_2Cl] 4 mg/L as Cl_2	[NH_2Cl] 8 mg/L as Cl_2
Cationic PAMS	11.38 ± 0.11	13.39 ±0.30
Mannich	> 112,000 ± 206	> 156,000 ± 24
PolyDADMAC	409 ± 70	598 ± 44
Polyamine	585 ± 18	968 ± 52

Table 5.2 Effect of monochloramine dosage on DMA concentration from the polymers. Reaction conditions: initial [NH_2Cl] = 4 and 8 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	DMA concentration (μg/L)	
	[NH_2Cl] 4 mg/L as Cl_2	[NH_2Cl] 8 mg/L as Cl_2
Cationic PAMS	2.29 ± 0.70	2.98 ± 0.71
Mannich	71.2 ± 4.5	90.0 ± 0.2
PolyDADMAC	30.7 ± 3.2	34.9 ± 0.6
Polyamine	26.8 ± 1.9	37.2 ± 0.0

5.2.5 Impact of Sequential Addition of Free Chlorine and Ammonia

Unlike the other previous experiments in which preformed monochloramine was used as the oxidant, free chlorine and ammonia were added sequentially to the polymer solution in these tests. The objective was to assess whether contact with free chlorine prior to ammonia addition for in-situ monochloramine formation could impact the potential of the polymers to yield NDMA. Initially, 4 mg/L (as Cl_2) free chlorine was added to the polymer solution. Subsequently, 0.9 mg/L (as Nitrogen) ammonia was added after 90 or 240 min to the polymer solution to form monochloramine. The reactions were allowed to undergo for 7 days, followed by analyses for NDMA and DMA concentrations. In these tests, although the initial monochloramine concentration was not known, the residual monochloramine after the reaction was found to be in the rage of 2.1-2.7 mg/L (as Cl_2) after the reaction, comparable to those in cases when 4 mg/L (as Cl_2) of preformed monochloramine was used as the oxidant.

As shown in Table 5.3, pre-exposure to free chlorine did not increase, but instead slightly decreased the polymers' NDMA yield. Extending this free chlorine contact time from 90 min to 240 min also did not result in increase in NDMA yield. In contrast, pre-exposure to free chlorine did increase the concentration of DMA released from the polymers compared to the cases without prior free chlorine contact (Table 5.4). However, longer free chlorine contact time did not increase the DMA release except slightly in the case of Mannich polymer. Contrary to the other experiments discussed earlier, this part of study presents a case with no corresponding relationship between the NDMA yield and the DMA concentration from the polymers.

Table 5.3 NDMA formation from the polymers after sequential addition of free chlorine and ammonia. NaOCl (4 mg/L as Cl_2) was first added to the polymer solution followed by addition of NH_3 (0.9 mg/L as N) after 90 or 240 min. Other reaction conditions: pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	NDMA Yield (ng/mg polymer)		
	Preformed [NH_2Cl] 4 mg/L as Cl_2	NH_3-N added after 90 min	NH_3-N added after 240 min
Cationic PAMS	11.38 ± 0.11	7.63 ± 0.15	8.51 ± 0.11
Mannich	> 112,000 ± 206	> 48000 ± 2233	> 54600 ± 3973
PolyDADMAC	409 ± 70	501 ± 21	541 ± 17
Polyamine	585 ± 18	525 ± 2	526 ± 5

Note: the results in the tests using 4 mg/L (as Cl_2) of preformed monochloramine (Table 5.1) are listed to compare with the results from the tests using sequential addition of free chlorine and ammonia

Table 5.4 DMA concentration from the polymers after sequential addition of free chlorine and ammonia. NaOCl (4 mg/L as Cl_2) was first added to the polymer solution followed by addition of NH_3 (0.9 mg/L as N) after 90 or 240 min. Other reaction conditions: pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	Measured DMA concentration (µg/L)	
	NH_3-N added after 90 min	NH_3-N added after 240 min
Cationic PAMS	3.03	3.05 ± 0.02
Mannich	179 ± 7	252 ± 1
PolyDADMAC	44.0 ± 6.4	43.4 ± 0.7
Polyamine	42.1 ± 3.7	44.0 ± 4.4

Note: DMA concentrations reported in Table 5.4 are the measured DMA concentration without correction with concentration factor or internal standard

CHAPTER 6

Conclusions

Four types of water treatment polymers (cationic polyacrylamide (cationic PAMS), aminomethylated polyacrylamide (Mannich), poly-diallyldimethylammonium chloride (polyDADMAC) and polyamine) were evaluated in aqueous solutions at circumneutral pH and room temperature to form *N*-nitrosodimethylamine (NDMA) upon exposure to nitrite, free chlorine, monochloramine or chlorine dioxide. High dosages of polymer and oxidant and long reaction time were employed in order to assess the maximum potential to form NDMA. In general, the NDMA formation potential followed the trend of Mannich >> polyamine ~ polyDADMAC > cationic PAMS. The concentration of the well-known NDMA precursor dimethylamine (DMA) in the polymer samples (without exposure to oxidant) also followed the similar trend above. Among the four oxidants, reactions with monochloramine resulted in the highest levels of NDMA while reactions with chlorine dioxide results in the lowest levels of NDMA in general. However, an unexpected increase in NDMA yield was observed with the presence of both chlorine dioxide and nitrite. The NDMA yield (in μg NDMA per mg polymer unit) and DMA concentration after reaction with monochloramine generally increased with increasing monochloramine dosage and contact, time, but decreased slightly with increasing polymer dosage. In sequential addition of free chlorine and ammonia to form in-situ monochloramine, contact with free chlorine prior to ammonia addition actually

decreased the NDMA yield compared to the cases with direct contact with preformed monochloramine, despite that increase of DMA concentration was observed. Overall this study provides an initial assessment regarding NDMA formation potential from the combination among four polymers and four oxidants. Based on the results of this study, further studies to investigate potential NDMA formation under conditions representative of water treatment plants (e.g., lower concentrations of polymers, shorter contact time with oxidant, etc.) and to elucidate the NDMA formation mechanisms from the polymers are necessary in order to discern the potential role of polymers as NDMA precursors in actual treatment systems and to develop strategies to minimize such potential contribution.

APPENDIX
Experimental Data

Table A.1 Polymers Screening in DI and Wastewater (WW) Matrices
Reaction conditions: Polymer concentration: 23.58, 0.88, 20 and 9.94 mg/L active, for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively; pH = 7; 23 ºC; reaction time = 24 hours.

Condition	Matrix	NDMA (ng/L)			
Matrix controls					
NO_2^- 20 mg/L	DI	< 15			
HOCl 10 mg/L as Cl_2	DI	< 15			
NH_2Cl 10 mg/L as Cl_2	DI	< 15			
ClO_2 8 mg/L as Cl_2	DI	< 15			
ClO_2 8 mg/L as Cl_2 plus NO_2^- 20 mg/L	DI	< 15			
ClO_2 8 mg/L as Cl_2 plus DMA 0.3 mM	DI	< 15			
		Cat PAMS	**Mannich**	**PolyDADMAC**	**Polyamine**
Polymer alone	DI	21.1	19.7	19.1	19.1
W/ NO_2^- 20 mg/L	DI	20.3 ± 1.2	113 ± 23	76.1 ± 22.9	25.3
	WW	52.0 ± 2.7	408 ± 73	130 ± 6	82.3 ± 0.9
W/ HOCl 10 mg/L as Cl_2	DI	21.1 ± 1.3	24.6	39.6	118 ± 27
	WW	99.4 ± 5.0	219 ± 27	104 ± 3.0	663 ± 8
W/ NH_2Cl 10 mg/L as Cl_2	DI	42.3 ± 0.6	> 52000 ± 11000	1719 ± 266	2243 ± 233
	WW	382 ± 24	> 400,000 ± 13000	2558 ± 729	4041 ± 257
W/ ClO_2 8 mg/L as Cl_2	DI	77.6 ± 0.8	96.0 ± 29.4	55.3 ± 2.8	60.5 ± 1.2
	WW	67.0 ± 5.0	166 ± 5	62.9 ± 9.4	61.2 ± 3.0
W/ ClO_2 8 mg/L as Cl_2 plus NO_2^- 20 mg/L	DI	367 ± 2	3455 ± 263	706 ± 53	546 ± 50
	WW	57.0 ± 0.1	743 ± 192	152 ± 8	122 ± 5
W/ ClO_2 8 mg/L as Cl_2 plus DMA 0.3 mM	DI	78.2 ± 7.5	114 ± 17	80.2 ± 38.6	70.7 ± 12.1
	WW	108 ± 5	187 ± 4	150 ± 20	156 ± 17

Table A.2 Impact of Polymer Dosage on NDMA Formation

Reaction Conditions: Polymer dosage x: 2.95, 0.11, 2.5 and 1.24 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively; NH_2Cl = 4 mg/L as Cl_2; pH = 8.6; 23 ºC; reaction time = 7 days.

Polymer concentration (mg/L)	NDMA (ng/L)			
	Cat PAMS	Mannich	PolyDADMAC	Polyamine
X	42.8 ± 2.9	> 10600 ± 196	1111 ± 43	1043 ± 98
2X	67.1 ± 0.6	> 24600 ± 45	2044 ± 350	1454 ± 45
4X	73.9 ± 2.8	> 48200 ± 1400	2576 ± 71	1960 ± 115

Table A.3 Impact of Monochloramine Contact Time on NDMA Formation

Reaction Conditions: Polymer concentration: 5.89, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively; NH_2Cl = 4 mg/L as Cl_2; pH = 8.6; 23 ºC; reaction time: 2, 4 and 7 days.

Contact time (days)	NDMA (ng/L)			
	Cat PAMS	Mannich	PolyDADMAC	Polyamine
2	51.0 ± 0.4	> 22100 ± 39	809 ± 28	964 ± 46
4	58.4 ± 0.3	> 23500 ± 186	1344 ± 43	1328 ± 44
7	67.1 ± 0.6	> 24600 ± 45	2044 ± 350	1454 ± 45

Table A.4 Impact of Monochloramine Dosage on NDMA Formation

Reaction Conditions: Polymer concentration: 5.89, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively; NH_2Cl = 4 and 8 mg/L as Cl_2; pH = 8.6; 23 ºC; reaction time = 7 day.

Monochloramine dose (mg/L as Cl_2)	NDMA (ng/L)			
	Cat PAMS	Mannich	PolyDADMAC	Polyamine
4	67.1 ± 0.6	> 24600 ± 45	2044 ± 350	1454 ± 45
8	78.9 ± 1.8	> 34300 ± 5	2989 ± 220	2405 ± 128

Table A.5 Impact of Sequential Addition of Free Chlorine and Ammonia on NDMA Formation

Reaction Conditions: Polymer concentration: 5.89, 0.22, 5 and 2.48 mg/L active for cationic PAMS, Mannich, polyDADMAC and polyamine, respectively; NH_4Cl = 4 mg/L as Cl_2; NH_3-N = 0.9 mg/L N; pH = 8.6; 23 ºC; reaction time = 7 day.

Free chlorine contact time prior to ammonia addition (min)	NDMA (ng/L)			
	Cat PAMS	Mannich	PolyDADMAC	Polyamine
90	45.0 ± 0.9	> 10500 ± 490	2504 ± 103	1305 ± 6
240	50.1 ± 0.6	> 11900 ± 872	2705 ± 84	1307 ± 11

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